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AND NATURAL GASOLINE MANUFACTURER

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Editor

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VOLUME 15, No. 11 NOVEMBER, 1936

REFINER
AND NATURAL GASOLINE MANUFACTURER
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The Look Box

THE current year has been marked by a revival of activity in construction of refinery processes, refining plants and natural gasoline plants to an extent that the total work has not been equalled by any year since 1929. Although 1936 has seen completion of a number of major programs of modernization and expansion, much work still remains for finishing in 1937. Further, many companies have spent their appropriations for 1936 and are now awaiting the turn of the year before entering into additional work.

Construction

An analysis of present trends in refining will show that progress demands still further improvement, expansion and general replacement of processes. In the cracking field, for example, a few companies have installed newer type of more efficient units during 1936, but there are many more where this work has not yet been undertaken. The combination type of unit which can process crude oil, crack the gas oils or reduced crudes and reform the naphthas at operating costs well below those secured by older cracking units will go into a number of refineries during the next few years.

Polymerization, for all of its "reported" hesitancy, is coming more rapidly than many believe. There has been apparently a growing feeling on the part of many in the industry that it would be well to wait until several of the units under construction and operating, from which performance records could be taken, before widespread activity in construction should be undertaken. However, reports from those engaged in licensing and erecting such units discredit such reports and indicate that many more concerns than is generally known are proposing construction of such facilities at much earlier dates than some would believe.

Increased activity in cracking unit construction and polymerization unit erection, coupled with some activity in distillation and vacuum distillation equipment has brought about a condition where materials are hard to get on the job. Many current programs have been held up because of difficulty in securing delivery of steel, refractories, piping, concrete, brick, and other essential items, it is reported. A condition of that nature, coupled with the usual "end of the year" slowing down and the usual preferance for building during the spring and summer months, contribute to an expected slowing down of activity over the coming winter. That it will be revived early in the spring of 1937 is a foregone conclusion, or else a great many men working over a mass of drawings are wasting time for a large number of companies.

Another field of activity where some commentators have been prone to feel that work was fairly well completed is that of solvent extraction and solvent refining, solvent deasphaltizing and other solvent process applications. A look into the field of activity, which has been mark-

edly important during the past two or three years, reveals that such construction in the lubricating oil department of the refineries of the world is but about 50 percent completed. There is to be a revival of construction of this nature in 1937.

The natural gasoline division of the industry, insofar as construction is concerned, took upon itself the task of erecting more plants this year and of improving more plants, than in any single year since the depression descended upon the country. The task of improvement is not yet complete. As in past years the new plants of 1937 will more than likely follow the drill, and where gas is available for processing, new plants will be erected.

Group Meetings

THE series of regional meetings of refiners sponsored by the manufacturing committee of the Western Petroleum Refiners Association which have been held during the past few weeks have proven of real value. Each of the district meetings held in Wichita, Tulsa, Fort Worth and Shreveport, have been well attended. In each district subjects have been chosen for presentation which were devoted to timely and interesting subjects in the respective territories. The invitation on the part of the association to all refiners, whether they were members or not, has been accepted. Reports from each of the four meetings of the series have been gratifying to the association, and those in attendance have stated that the group sessions were well worth while. This action on the part of the association and on the part of those giving their time to the preparation of the papers, is certainly commendable. There should be no question but that the periodic holding of these regional meetings should be continued, as no doubt they will be.

The experience of the former Louisiana-Arkansas Refiners Association, now the Ark-La-Tex division of the Western Petroleum Refiners Association, which group has been holding monthly technical meetings in Shreveport and El Dorado during recent years, points to the value which can be received by these frequent sessions for interchange of ideas. Likewise the monthly meetings of the California Natural Gasoline Association, which have been in progress for the past several years, denotes that sustained interest can be secured. Men like to get together and exchange views. The value to be secured from such meetings is easily measured. Management should sincerely endorse such programs and not only permit attendance upon the part of the men, but insist upon it.

The recent Western Petroleum Refiners Association meetings have been interesting. At these sessions men well qualified to speak have presented for discussion valuable papers dealing with such subjects as desalting of crudes, the trend in cracking process design and operation, motor fuels from catalytic treatment of cracked gases, thermal polymerization, balloon vapor recovery systems, color stability of gasoline, economics of gasoline versus tractor fuel, corrosion of heat exchangers and condenser tubes, petroleum testing methods, gum inhibitors, clay treating processes, disposal of refinery wastes, and furnace design. Such a line-up of timely and interesting topics augurs well for future efforts along these lines. And the rapid progress in engineering and technical development in this industry makes for real and lasting value being secured from such gatherings.

On Taxes

"AT TIMES we are inclined to feel that the industry is thoroughly conscious of its terrific tax burden. However conscious we may be, we are brought face to face with facts developed from time to time which should shock not only every member of the industry, but all its customers as well.

"Recently the American Petroleum Industries Committee, utilizing census figures and tax data, revealed that roughly one third of service-station income is collected for governments—local, state, and federal—in taxes. This figure standing by itself may not immediately appear startling; but, when its significance is appreciated, it should give everyone pause for thought. Those who are engaged in serving the public with petroleum products do so in the hope of making a return therefrom. They invest their time and funds to obtain that return; yet virtually every third dollar of their gross revenue is taken by government in taxes. To put it another way:—measured by the return, a third of the investment, a third of the work, a third of the time yields revenue exclusively for government.

"It is hoped that employees will understand how taxes affect their employment and income. Ultimately, the amount of productivity must govern employees and employment. One third of the employees' productivity is taken by taxes. The average tax load is about $1,222 per petroleum-industry employee per year. With the census figures revealing that for each $4,700 of business service stations, on the average, give employment to one worker (either proprietor or paid employee) it is possible that work for 187,000 additional employees could have been provided by the tax moneys. Indirectly, addi-

(*Continued on page 55a*)

The Problem of the

Rational Utilization of Petroleum *and of* Petroleum Distillates

V. N. IPATIEFF
Universal Oil Products Co.
Research and Development Laboratories

VLADIMIR N. IPATIEFF, *of the Universal Oil Products Company, Riverside, Illinois, delivered the accompanying paper at the Division of Refining group session Wednesday morning, November 11, in connection with the American Petroleum Institute's Seventeenth Annual Meeting at Chicago.*

Dr. Ipatieff began research work in catalytic reactions under high pressures with organic matters in 1900, working in the laboratories of the Academy of Artillery at St. Petersburg (now Leningrad), Russia. He successfully undertook original research in separating metals from solutions by means of hydrogen. In 1905 he introduced high pressures in polymerization of ethylene and other olefins. Continuing his studies of polymerization in the presence of various catalytical agents, Dr. Ipatieff found an agent which permits of the transformation of a portion of the gases from the cracking operations, containing olefins, into high-octane gasoline.

Dr. Ipatieff, after graduating from the Academy of Artillery, served in the World War with the rank of general. He was in charge of all chemical work for the Russian government. He is a Commander of the Cross of the Legion of Honor, and has other decorations. He is a member of numerous scientific societies throughout the world, and also of the faculty of Northwestern University.

FOLLOWING the history of the petroleum industry from its very beginning, nearly a hundred years ago, when the Dubinin Brothers[1] made their first attempts to distill kerosene from petroleum, it is possible to divide its development into distinct periods.

These periods were determined by the fuel market and by the applications of petroleum distillates in other branches of industry.

Petroleum quickly found a wide application in industry as a fuel. But since illuminating oils and high-boiling products such as lubricating oils were also desired, it became necessary to work out improved methods for the distillation of petroleum, leaving for fuel only the residues which could not be used for other purposes.

THE DISTILLATION PERIOD

This first period of the development of the petroleum industry can be called "the distillation period," and it lasted from the sixties of the last century to the beginning of the World War.

During this time the attention of the technologists was concentrated upon the fractional distillation of petroleum and the purification of its distillates. The chemistry of petroleum was in an embryonic state, and the industry was not interested in it. The main objects were the production of petroleum and the discovery of its underground reserves — problems suited to engineers and geologists rather than chemists.

It may be worthwhile to give an example of the lack of interest shown by the leading oil men of Russia in a more rational utilization of petroleum. In 1911, I was consultant to Nobel Brothers Company; and I suggested, together with Gurwitsch, their chief chemist, that they study the cracking of certain petroleum fractions for which there was no demand. The executive board replied that they were willing to furnish the means for doing this research in my laboratory at the Artillery Academy, but that they did not see much practical value in the subject. Such an answer was justified from a commercial point of view, since oil companies at that time were making huge profits by merely selling "straight-run" distillates.

However, leading chemists began to be interested in the composition and origin of petroleum. Mendeleeff was the first to realize the tremendous importance of petroleum as a potential source of organic compounds. Knowing that geological investigations cannot give definite figures concerning the actual amount of the oil reserves in any locality, he gave a warning that petroleum is too valuable to be used chiefly as fuel.

Markovnikov was among the first to study the composition of various petroleums. He proved that Baku oil contains naphthenes, i.e., hydrocarbons with a ring structure, which differed from the open-chain paraffin hydrocarbons found in Pennsylvania oil.

Numerous investigations made during this time in the United States, Russia, and other countries concerned themselves not with the chemistry of petroleum, but rather with its technology.

The reason for the lack of study in petroleum chemistry was mainly the chemical inertness of paraffinic and naphthenic hydrocarbons. The benzene hydrocarbons found in coal tar differ greatly from the petroleum hydrocarbons. The benzene hydrocarbons

are reactive, and by the methods of organic synthesis could be readily converted into valuable products such as dyes, drugs, and explosives.

The study of petroleum chemistry was brought on by the World War and by the development of high-power engines for the automobile industry, and later for aviation.

The production of gasoline by ordinary distillation of petroleum had become inadequate. This was first felt during the war, and it was at this time that the cracking process, i.e., thermal decomposition of petroleum with the purpose of increasing the proportion of low-boiling constituents at the expense of the high-boiling ones, received considerable attention in the United States.

THE CRACKING PERIOD

In Russia, during the war, tremendous quantities of petroleum were subjected to pyrolysis, and thousands of tons of aromatic hydrocarbons (benzene, toluene, and xylene) were produced for the manufacture of explosives.

This period in the development of the petroleum industry can be called "the cracking period," because the cracking process in a short time found broad application in the United States and later in other countries. Present conditions of the petroleum market are such that it is profitable to crack a high percentage of crude petroleum, since the cracking process makes it possible to obtain up to 70 percent yields of good gasoline.

Although, at first glance, the reactions involved in the thermal decomposition ("cracking" and "pyrolysis") of petroleum hydrocarbons may appear to be simple, in reality they are very complex—because numerous reactions take place simultaneously.

The development of the petroleum industry gave the impulse to scientific chemical research in this field. It had become necessary not only to determine the most favorable factors of time, temperature, and pressure for the cracking of various kinds of oil, but also to begin research on the actual reactions taking place in cracking. There are two dominating reactions in the cracking process: 1, decomposition of hydrocarbons into fragments and dehydrogenation; 2, re-combinations or secondary reactions. These two main reactions attracted the main attention of chemical thought.

In the laboratories of the United States, and to some extent in other countries, numerous investigations were made on the thermal decomposition of individual hydrocarbons of various kinds, particularly paraffins. These interesting investigations indicate the trend of thought of chemists in determining the manner in which hydrocarbon molecules decompose under high temperatures.

In this, research effort was made to determine the strength of various bonds between carbon and hydrogen and carbon to carbon in hydrocarbons of various structures, and to develop a "theory of the radicals" which would make it possible to predict from thermodynamic calculations the manner in which molecules of a given hydrocarbon would break at a given temperature.

It cannot be denied that abundant scientific material has been collected during recent years in connection with the study of the thermal decomposition of hydrocarbons which gives us valuable information, theoretical and practical, concerning the stability of various hydrocarbons. This also leads us to new ideas concerning the more rational utilization of petroleum hydrocarbons, so as to obtain from them hydrocarbons with more valuable properties and to convert them into other classes of organic compounds.

THE CATALYTIC PERIOD

Industrial organic chemistry, watching the development of the petroleum industry during its second or "cracking" period, soon took notice of the profits which could be made by utilizing the products of cracking as starting material for organic synthesis.

The first to be utilized were the olefins in cracked gases, which were converted into alcohols, ketones, etc.; but we now face the important question whether, under present conditions of the market and of other branches of chemical industry, we can stop at this stage of the development of petroleum products and with these methods which now are almost generally accepted.

My purpose is to answer this question, and to show that at the present time we are entering the third period of the development of the petroleum industry, which should be called "the catalytic period."

In order to show the necessity and usefulness of introducing new catalytic methods in the petroleum industry, I shall illustrate by an example from organic technology, which will immediately show you the advantages which could be obtained by substituting a delicate catalytic method[2] for a rough thermal one.

Thirty-five years ago no one could explain why the pyrolysis of alcohols at 400-600°C. yields various products such as hydrogen, carbon monoxide, aldehyde, methane, etc.

The thermal decomposition of alcohols, especially ethyl and *iso*amyl alcohols, had been studied by many outstanding chemists for almost 100 years, but not one of them could explain in what way the decomposition took place and why such diverse products were obtained.

However, after the author had discovered that certain catalysts influence the decomposition of organic compounds at high temperatures, it was possible not only to understand the exact manner in which the decomposition proceeds, but also to obtain selective action by various catalysts.

We were able to establish, from the very beginning of our investigations, that some metals and their oxides promote "aldehyde" decomposition of alcohols; that other oxides promote "ethylene" decomposition; and that still other oxides make it possible to obtain diolefins from the alcohols.

A catalyst causes the decomposition of an organic compound to take a certain direction, due to its specific chemical and physical properties. Taking into consideration the most vital problems facing the petroleum industry, we believe that a new period of its development has begun, viz., the catalytic period.

The necessity of introducing catalysis for obtaining various products from petroleum is evident from both the scientific and the economic points of view. We know that catalytic methods have great advantages, and they already occupy a firm place in chemical industry.

In the petroleum industry they will be perhaps even more important, since the reserves of this valuable raw material should be conserved by using them to better advantage. Therefore, the more rational utilization of petroleum constitutes a problem of

great importance for the chemist as well as for the engineer.

You are well aware of the controversy concerning the extent of the petroleum reserves in the earth. This question, of course, is closely connected with the hypothesis of the origin of petroleum. I think that I am not mistaken in saying that the majority of chemists, geologists, and biologists accept the organic hypothesis of the origin of petroleum.

Have we sufficient ground to form conclusions as to the actual amount of the petroleum reserves? This has an important bearing on the rational utilization of crude oil. This question divides geologists and chemists into two groups. Some[3] consider that the petroleum reserves are very limited, and that in the United States there will be enough for only 5 to 8 years. Others[4] insist that the petroleum reserves have been carefully estimated, and that there is no danger of shortage in the immediate future.

We think that both sides have arguments worthy of consideration.

Those who say that the petroleum reserves are small induce us to regard the use of it as fuel, as well as raw material, with greater care.

On the other hand, the data presented to prove that we possess enormous reserves of petroleum are not convincing. All previous estimations of the oil reserves in the Baku region proved to be wrong.[5] Economic methods of utilization must, therefore, be chosen; and, for this reason, catalysis must be introduced into the petroleum industry.

In order to convince you that the catalytic period has become a reality, we shall mention several catalytic processes which are in commercial operation.

Figure 1 lists the most important types of catalytic reactions of the various hydrocarbons found in petroleum. These reactions at the present time are being investigated in various scientific and research laboratories.

FIGURE 1
Catalytic Reactions of Various Petroleum Hydrocarbons

We are in a position to say that all reactions listed in Figure 1 will find broad application in the petroleum industry. Our laboratory experiments fully justify this statement.

Some of these reactions, viz., straight polymerization[6] and also selective and mixed[7] polymerization, are already applied on a large scale; and hundreds of thousands of barrels of excellent gasoline, with high octane number, are being produced in the United States by these reactions.

Although the method of polymerization of olefins under pressure,[8] and without the use of a catalyst, is also employed in some plants, a careful consideration of the comparative merits of these two methods brings us to the conclusion that the catalytic method has numerous advantages over the method where temperature and pressure alone are used.

No one can deny that with the use of a catalyst we are able to produce, by means of selective polymerization and catalytic treatment of olefins, a very good yield of special gasoline for aviation. This gasoline has an octane number of about 100, without addition of any tetraethyl lead.

Polymerization at high pressures and temperatures, but without a catalyst, cannot produce such a good yield of aviation gasoline. Catalytic methods, with a carefully-selected catalyst, are sometimes actually capable of producing theoretical yields—which has never been possible by pyrolysis. Catalytic methods permit us to select from the mixture of substances only those which we need, without ruining the others which can be subsequently utilized for polymerization.

When pyrolysis of paraffins, rather than catalytic dehydrogenation, is employed for the production of olefins, all the experiments and calculations show that the yield of the olefins is considerably lower, and that the hydrogen is contaminated by such gases as methane, ethane, etc., which diminishes its value for hydrogenation.

Another new and important catalytic reaction investigated in our laboratory is the direct alkylation of paraffins and naphthenes by the olefins.[9] This reaction is superior to the Friedel and Crafts reaction, which requires a preliminary preparation of alkyl halides and makes it possible to introduce the radicals into the molecules of certain hydrocarbons only through their agency.

For example, the alkylation of *iso*butane produces directly a good yield of *iso*octane having a high octane number. By this method we can produce various saturated hydrocarbons of *iso*structure, such as *iso*heptane, *iso*decane, etc. Data obtained in our laboratory give us the assurance that this process of synthesis of high-octane-number paraffins could be utilized on a commercial scale. The advantages of this method are obvious. Further investigations of this reaction undoubtedly will make it possible to commercialize this method, and we hope that the future industry will adopt it.

To further emphasize the importance of catalytic methods for the petroleum industry, we can compare the present "reforming" process for increasing the octane number of gasoline with proposed catalytic methods of auto-destructive alkylation and catalytic *iso*merization of hydrocarbons.

Undoubtedly, the reforming process considerably improves the quality of gasoline; but, as with any pyrolysis, it is accompanied by the formation of gases such as methane, ethane, etc., and of other normal paraffins.

By merely subjecting hydrocarbons to further pyrolysis, we cannot utilize them as efficiently as by catalytic reactions with other hydrocarbons.

The more delicate method of catalytic destructive

alkylation will allow us to treat saturated hydrocarbons in such a way that the gasoline produced will have a high octane number, and the gases will contain a very important hydrocarbon, *iso*butane, which is so desirable for alkylation. In the future the by-products of petroleum will be utilized in a more efficient manner, and all waste will be eliminated.

Cracking, which at the present time is applied on such a large scale, will probably be modified by the introduction of catalysis. Since the various hydrocarbons contained in petroleum will require different conditions of time, temperature, pressure, etc., for catalytic decomposition and *iso*merization, it is probable that "selective catalytic cracking" will be necessary—starting with specific distillates for each operation.

I shall not discuss, in this article, the high-boiling petroleum distillates from which lubricating oils are obtained. This branch of the petroleum industry has employed for a number of years the catalytic method of destructive hydrogenation for the purpose of obtaining good lubricating oils from petroleum distillates which otherwise had no application in industry. Also, the catalytic polymerization of olefins to synthetic lubricating oils, by means of active catalysts such as aluminum chloride, is being used.

The above examples are sufficient to convince us that further progress in the petroleum industry must be achieved by the introduction of catalytic methods so that this precious raw material, petroleum, which exists in the earth in limited quantity, may be utilized in the most rational manner. Recent scientific and technical publications, particularly in the United Sates and Russia, confirm the arrival of the "catalytic period" in the development of the petroleum industry, and it is evident that chemistry will be increasingly important.

Science does not stop in its development; and we may expect that, simultaneous with the growing application of catalysis in organic chemistry, there will appear new ways for the synthesis and decomposition of organic compounds.

I have in mind the role played by the ferments and enzymes, the so-called organic catalysts. Many such processes are being conducted on a large scale.[10]

It has been shown by Omelyanski[11] that the stable organic compounds, cellulose, can be decomposed in two different directions by two different ferments. One of the decompositions yields hydrogen; and the other, methane. This selective fermentation is the product of the life processes of two organisms, and requires no other energy. It may be possible to find such ferments which will produce with petroleum hydrocarbons the reactions which are now carried out thermally and catalytically. From the material now available in this field of vitalism, we see that these processes are very economical and simple. Certainly, this is a method for the distant future. First, our laboratories and plants must develop and apply the methods of inorganic catalysis. At present we can only dream of vitalistic processes in the field of hydrocarbons.

Let us hope that in the future the petroleum industry will make good use of these methods of vitalism, just as at the present time it has successfully begun to apply the methods of inorganic catalysis in its processes.

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Pressure tanks for light fractions of natural gasoline, Texas Panhandle.

The Stability of Residual Fuels

A. H. BATCHELDER
Standard Oil Company of California

ABSTRACT

STABILITY of residual fuels under service conditions is of great importance, particularly the tendency to coat heater coils with a deposit which retards heat transfer. Conventional physical tests and inspections do not offer a satisfactory means of rating or grading fuels in this respect.

An apparatus and procedure are described which permit the prediction of this service characteristic. The method is exceptionally valuable in connection with the utilization of cracked fuel oils and of blends of these with straight-run residuum and cutter stock. Theoretical aspects of fuel-oil blending are discussed and illustrated by typical examples.

THe first fuel oils available in commercial quantities consisted of residua from which gasoline and kerosene had been distilled, and occasionally of untopped crude oils. The rise in the demand for gasoline which accompanied the advent of the automobile was at first amply met by increased production of crude oil brought about by the more extensive drilling of oil wells, by advances in drilling technique, and by the discovery of new oil fields. Expansion in the production of gasoline, therefore, resulted at first in a corresponding increase in the volume of residual stocks available for industrial fuel.

The acceleration in the demand for gasoline continued at such a rate that serious shortages would have occurred had it not been for the development and adoption of cracking processes as a means for increasing the yield of lighter fractions from crude. The already rapidly increasing proportion of gasoline produced by cracking less volatile stocks has in recent years received further impetus from the demand for cracked gasolines per se, because of their favorable combustion characteristics in modern high-compression engines. It is probable, too, that the growth of cracking operations will inevitably result in almost complete withdrawal of straight-run residuum stocks from use as industrial fuels.

A. H. BATCHELDER, of Standard Oil Company of California, Richmond, California, read the accompanying paper at the Division of Refining group session Wednesday morning, November 11, in connection with the American Petroleum Institute's Seventeenth Annual Meeting at Chicago.

Mr. Batchelder was graduated in 1927 by the College of Chemistry, University of California, and for three years engaged in research on drying oils and resins. He entered the employ of Standard Oil Company of California in 1930 and has since been engaged mainly in research on fuels and asphalts.

Displacement of straight-run by even severely-cracked fuels of proper stability characteristics is in no respect disadvantageous to consumers of fuel oil. Whatever prejudice there exists against the use of cracked fuels has resulted from sedimentation and heater-coating difficulties which are experienced with unstable fuels. The persistence of such prejudice is reflected in the present emphasis upon high gravity, which is in itself of little significance as a criterion of fuel oil quality; in fact, the necessity for meeting minimum gravity specifications is in many cases responsible for the production of unstable blends from satisfactory cracked tar fuels. The main disadvantage attaching to the use of cracked stocks lies in the inability of the consumer, and frequently of the refiner, to distinguish between unstable and satisfactory fuels.

Because of the large navy fuel requirement, the development of a specification which will permit acceptance of deeply-cracked fuels of suitable stability characteristics is of the utmost importance and, because of the present fleet concentration, is of particular interest to the petroleum industry on the Pacific Coast. The problem of navy fuel supply is complicated by the fact that the greatly accelerated demand for fuel, which would be the accompaniment of intensified naval operations, would probably coincide with increased gasoline and fuel-oil requirements due to correspondingly enhanced industrial and possibly military activities. Under such circumstances it is not improbable that shortage or insecurity of water transport, and the time element involved, might make it necessary for the total navy fuel requirement to be obtained on short notice from the nearest supply point.

THEORETICAL CONSIDERATIONS

STRAIGHT-RUN FUELS

Crude oil, maintained at the temperature at which originally stored in the ground, is free from suspend-

ed matter other than dirt, water, and salts which may properly be considered as foreign material; all of the hydrocarbon material exists in solution. Parenthetically, the term "solution" will be understood to be used in the popular sense to describe highly-saturated or protected dispersions not separable by filtration or the ordinary laboratory super-centrifuge. Any suspended hydrocarbon material which might be present in the oil in underground storage would be expected to be filtered out in the passage through the oil-bearing formations. The character of the asphaltic matter obtained in a given crude may be due to the solvent (or protective) properties of the oil as well as to the condition of the crude in underground storage. As the over-all solvent power of even the most naphthenic crudes is not very high, only easily dissolved asphaltenes occur in crude oils. Some crudes require the addition of only a small proportion of light naphtha to initiate precipitation of the heaviest asphaltenes present; cooling also may result in separation of wax as well as asphaltic matter.

Removal of gasoline and kerosene fractions by distillation greatly increases the stability of the heavy oil and asphaltic constituents, and imparts to them a considerable tolerance for even cutter stocks which might cause precipitation when added in small amounts to the crude. In general, straight-run residual fuels can be mixed with one another and with stocks as light as kerosene distillate without danger of precipitating asphaltenes. Their stability or tolerance for light cutter stocks is greater at higher temperatures. Fuels made by topping crudes or by cutting back straight-run asphalts, therefore, cause neither heater coating nor difficulties with sedimentation (other than wax or foreign material) on storage.

CRACKED FUELS

Prolonged exposure of oils to high temperatures results eventually in the attainment of an equilibrium between elementary carbon, hydrogen, and methane. However, as cracking is ordinarily carried out, oils are exposed for only a short time to temperatures above that at which thermal decomposition is rapid, resulting only in the splitting and dehydrogenation of hydrocarbon molecules. Part of the unsaturated compounds so formed are highly unstable and polymerize rapidly, so that cracking results in the formation of stocks both heavier and lighter than those present in the original charging stock. The exact composition of a cracked tar depends at least as much upon the character of the charging stock and the operating conditions as upon the severity of cracking.

From the standpoint of utilization in fuel oils, the essential difference between cracked and straight-run tars lies not in the lower gravity of the cracked product, but in its content of asphaltenes less soluble in organic solvents than the least soluble asphaltenes occurring in crude oils, and especially in the presence of small amounts of non-solvated or suspended hydrocarbons. These latter are sometimes called carboids. Because of the presence of difficultly-soluble asphaltenes, cracked tars are markedly less compatible with cutter stocks than straight-run residua, their sensitivity being such that in many cases sedimentation and heater-coating characteristics are more dependent upon the quality of the blending stocks than upon that of the cracked tar.

In any classification of asphaltenes in accordance with apparent solubilities, it should be kept in mind that the behavior of any given species of asphaltic compounds is greatly influenced by essentially foreign considerations, such as state of aggregation and the presence or absence of a protective agent.

Although the same general considerations govern both sedimentation and the formation of carbonaceous incrustations in fuel-oil heaters, the causes may be quite different. Sedimentation is due to the presence of suspended material in the fuel. Fuels containing heavy asphaltenes which are insoluble at ordinary temperature, and for that reason potentially dangerous from the standpoint of sedimentation, may be homogeneous at temperatures encountered in fuel-oil heaters, and may cause no heater coating. The substance responsible for the formation of deposits in heater tubes must be insoluble in oil at relatively high temperatures, whether already in suspension or formed in the heater.

Analyses of the material removed from cracked fuels at 200° to 300°F. by filtration or super-centrifuging show it to be substantially identical to the material deposited in fuel-oil heaters. The essential constituent is a heavy coke-like, hydrocarbon material, insoluble in benzol at room temperature. It is significant, too, that the solvent power of benzol for heavy asphaltenes is not very different from that of cracked gas oils at the temperatures usually encountered in fuel-oil heaters. It was observed also that fuels free from benzol-insoluble material cause no deposition in fuel-oil heaters, no matter what the stability at asmospheric temperature. It was, therefore, concluded that the benzol-insoluble content is a measure of the heater-coating potentialities of a cracked tar. The extent to which deposition has taken place can be precisely measured by weighing the deposited benzol-insoluble material after separation from the absorbed and adhering liquid fuel.

HEATER TESTS

The actual rate of deposition of benzol-insoluble material is dependent upon the characteristics of the cracked tar from which the fuel was made and the type and amount of diluent or cutter stock, and is not predictable from the usual inspections. The deposition rate is also affected by the design of the heater, the temperature of the heating surface, and the rate of flow. In order to study the heater-coating tendencies of fuels as a function of composition, it was found advisable to construct small easily-standardized test heaters.

These heaters were operated according to a standardized procedure. As deposition takes place unevenly at first, four days was chosen as the standard test period. The heaters are operated at moderate temperatures; because, although the rate of deposition increases markedly with temperature, more reproducible results are obtained at 350° to 400° F. than in the range from 400° to 600° F. The heaters themselves consist of tubes 0.70 inch in diameter, heated by steam at 135 pound pressure (gage) and immersed in the oil under test. The oil is contained in a vessel, which is itself immersed in a water bath. The space from which the deposits are removed is 0.115 square feet in area. The carbonaceous incrustation and adhering or absorbed oil are washed off with benzol, and the benzol-insoluble material filtered off and

weighed. The result expressed in grams is termed the "heater-coating index."

With most cracked fuels the results were found to be reproducible to closer than 10 percent. The advantage of weighing rather than measuring the deposit lies in the fact that a layer only a few ten thousandths of an inch thick contains a weight of benzol-insoluble material well within the range of an analytical balance.

The construction of the equipment and the operating procedure employed in the determination with heater-coating indices are described in the accompanying appendix.

CORRELATION WITH SERVICE CONDITIONS

In order to compare heater-coating indices with deposition rates in larger equipment over long periods, heater coils with a surface area of 1.95 square feet were installed near the bottom of 100-gallon

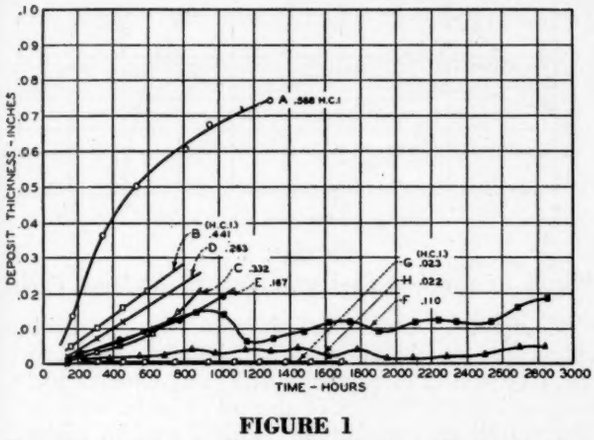


FIGURE 1
Deposition Rate for Fuels with Various Heater-Coating Indices.

containers. The coils were heated with saturated steam at 140 pounds per square inch (gage) and the oil maintained at 190° to 200°F. by a spray of cold water on the outside of the container. Sufficient of each stock under test was set aside to enable frequent

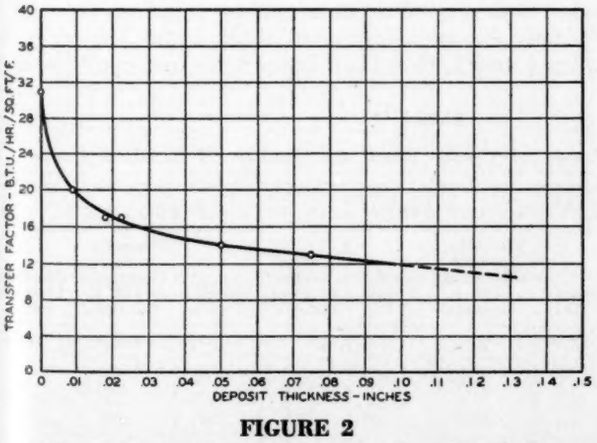
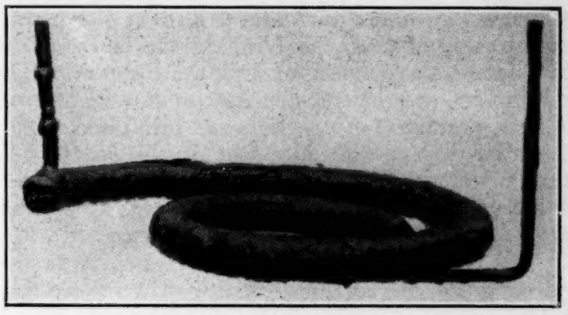


FIGURE 2
Effect of Heater Deposits upon Transfer Factor.

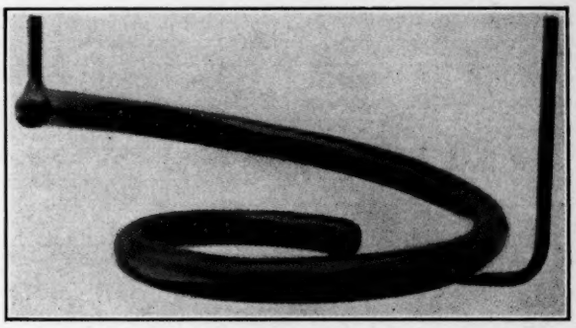
and regular replacement. The coils were removed from time to time for examination. The compositions of the fuels covered a wide range, although none with spectacularly high heater-coating indices was included. That reasonable correlation was obtained may be seen from the data in Figure 1.

The heat-transfer coefficient was measured by immersing the coils in fuel oil contained in a water-jacketed calorimeter. The steam was turned on and water circulated through the jacket at such a rate that its average temperature approximated that of the ambient atmosphere. The transfer coefficients so obtained are shown in Figure 2. It is of interest to note that a deposit of 0.1 inch reduced the transfer coefficient to 39 percent that of a clean coil.

It is particularly significant that scaling of deposits formed by fuels with both high and low heater-coating indices began at approximately the same time, with the result that fuels with low heater-coat-



Fuel "A." Heater-Coating Index—0.568. Hours—1,259



Fuel "G." Heater-Coating Index—0.023. Hours—1,690.

FIGURE 3

ing indices failed to build up appreciable deposits—indicating that there is no essential difference in the heater-coating characteristics of fuels with zero and reasonably low heater-coating indices; this is illustrated by the photographs (Figure 3) of heater coils employed in the large-scale tests. Data obtained from a limited number of tests conducted in large storage tanks were in every case in agreement.

Inasmuch at the actual rate at which heaters become coated depends upon the temperature and rate of flow at which operated, the heater-coating index must of necessity be regarded as an empirical measure of the coating tendency of a fuel. It has been observed that with the heated surface at 500°F. the rate of deposition may be five times as great as at 360°F., while at 300°F. the heater-coating rate is but from one-fourth to one-sixth that at 360°F. The effect upon heater coating of changes in rate of flow has been measured quantitatively in only a few cases; in the region of viscous flow, increasing the rate of

flow ten-fold has been observed approximately to halve the heater-coating rate.

REFINERY BLENDING PROCEDURES

The wide differences which exist in the chemical characteristics of cracking-still charging stocks, and in methods of processing and blending the resulting fuels, make it almost impossible to discuss adequately all of the variables involved. A few examples will, however, be given as a basis for discussion of the more important factors.

RELATION OF CUTTER-STOCK QUALITY TO HEATER DEPOSITS

The effect of additions of gas-oil cutter stocks to a cracked tar which has a low heater-coating tendency is shown in the data of Table 1 and in Figure 4. It will be observed that the cracked tar is compatible with a large proportion of low-aniline-point cutter (which lowers the heater-coating tendency) and with a moderate amount of cracked gas oil. The tolerance for the virgin gas oil is exceedingly small. High heater-coating indices may, therefore, be expected to accompany the use of straight-run cutter stocks or of excessive amounts of even cracked gas oil.

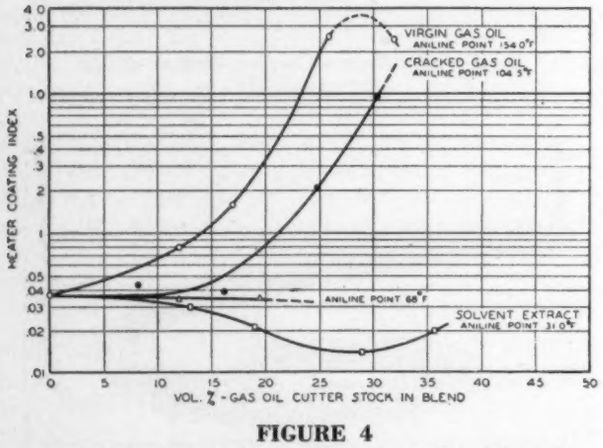


FIGURE 4

Heater-Coating Indices—Blends of Gas Oil and Cracked Tars.

It is of particular significance that, for fuels of any given viscosity manufactured as above, the lower-gravity stocks are to be preferred. Also, with any but cutters of unusually high solvent power, greater stability may be expected from higher-viscosity fuels. It should be noted (Figure 4) that, with progressive additions of low-solvent-power stock to even a stable cracked tar, the heater deposits increase to a maximum and then decrease—due to rapid sedimentation of heavy asphaltenes along with the benzol-insoluble material.

While all cracked tars behave in much the same general manner, the magnitude of the changes and the degree of compatibility depend upon the solvent or protective action of the oil constituents of the tar and the content of benzol-insoluble material. Higher-viscosity (molecular-weight) gas oils have a less marked effect (in either direction) per unit volume added, which tends to offset the effect of the greater volume which must be added to bring the tar to the desired viscosity.

OTHER BLENDING STOCKS

Residual asphalts lower markedly the heater-coating tendencies of cracked fuels to which they are added, and may even impart a considerable tolerance for cutter stocks with which the pressure tar may normally be incompatible. The magnitude of the decrease is such that it must be ascribed to a protective rather than to solvent action or dilution.

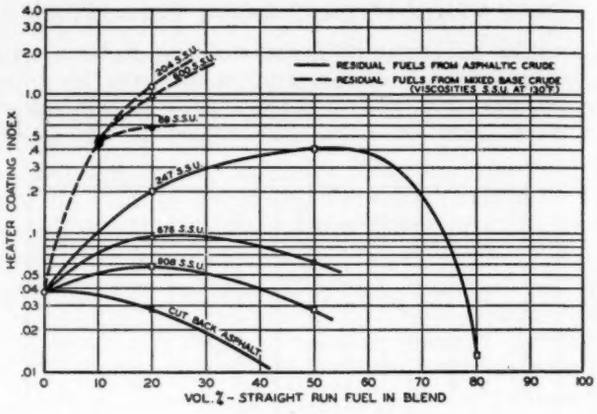


FIGURE 5

Blends of Cracked Fuel with Topped Residual Fuels.

The effect to be expected from topped residuum fuels, therefore, depends upon a balance between the protective action of the asphaltic constituents and the precipitating tendencies of the oil vehicle. This effect is illustrated by the data in Table 2 and in Figure 5. A cracked tar fuel with a low-heater-coating index was blended with fuels ranging from lightly-topped residuum to asphalt, made from the same asphalt-base crude, and with two topped residua from a much more paraffinic crude. It will be observed that the blending characteristics of straight-run fuels made from the asphalt-bearing crude are greatly improved as the viscosity is increased. Fuels made from the more paraffinic residuum are much inferior blending stocks, and very little changed by topping.

It may be of interest to note, from the data in Tables 1 and 2, that fuels from even one crude source

TABLE 1

Effect of Solvent Power of Cutter Stock on Quality of Cracked Fuels

	CUTTER-STOCK TESTS				FUEL TESTS		
	Gravity (° API)	Viscosity, Saybolt Universal, at 130° F. (Seconds)	Aniline Point (° F.)	Cutter Stock in Fuel (Percent)	Gravity (° API)	Viscosity, Saybolt Universal, at 130° F. (Seconds)	Heater-Coating Index
Cutter Added	.....	.....	.....	.....	5.9	3,353	0.037
Low-Aniline-Point Gas Oil	17.8	37.5	31.0	12.9	7.5	1,030	0.030
	17.8	37.5	31.0	19.2	8.2	650	0.021
	17.8	37.5	31.0	28.8	9.1	330	0.014
	17.8	37.5	31.0	35.6	9.8	220	0.020
Cracked Gas Oil	29.9	34.0	104.5	11.0	8.2	1,010	0.042
	29.9	34.0	104.5	16.4	9.2	610	0.039
	29.9	34.0	104.5	24.6	11.2	300	0.208
	29.9	34.0	104.5	30.4	12.3	210	0.905
Virgin Gas Oil	34.8	35	154	11.7	8.9	1,000	0.079
	34.8	35	154	17.1	10.2	610	0.158
	34.8	35	154	25.7	12.5	300	2.540
	34.8	35	154	31.7	14.0	220	2.412

TABLE 2

Blending Characteristics of Straight-run Residual Fuels

COMPOSITION	STRAIGHT-RUN FUEL		Straight-Run Added (Percent)	BLENDED FUELS		
	Gravity (° API)	Viscosity, Saybolt Universal, at 130° F. (Seconds)		Gravity (° API)	Viscosity, Saybolt Universal, at 130° F. (Seconds)	Heater-Coating Index
Residual Fuel Added.....	....	....	..	11.1	971	0.037
Topped Asphaltic Residuum.....	18.8	247	20	12.5	710	0.197
	18.8	247	50	14.8	451	0.392
	18.8	247	80	17.4	312	0.0135*
	15.8	676	20	12.0	900	0.092
	15.8	676	50	13.3	826	0.061
	15.1	908	20	11.8	1,014	0.057
	15.1	908	50	12.4	1,025	0.028
Asphalt Cut Back with Cracked Gas Oil.....	14.9	277	20	11.7	733	0.028
	14.9	277	80	14.0	342	0.006
Topped Mixed-Base Crude.....	24.0	89	10	12.2	842	0.450
	24.0	89	20	13.4	588	0.560
	22.7	204	10	12.0	921	0.445
	22.7	204	20	13.2	769	1.090
	19.0	401	10	11.7	1,031	0.476
	19.0	401	20	12.5	911	1.060
	11.0	600	10	11.0	1,000	0.476
	11.0	600	20	11.0	957	0.973

* Very unstable. Heavy asphaltenes settled shortly after blending.

may have almost any combination of gravity and heater-coating characteristics.

A GENERALIZED CASE

Figure 6, without scale, may be initially taken to represent the effect upon heater-coating characteristics of additions of low-solvent-power cutter stock to a cracked tar of good quality. The cracked tar and blends with moderate amounts of cutter would be represented between **A** and **B**. Excessive amounts of cutter, or the use of a highly-paraffinic stock, would result in high heater-coating tendencies, range **BC**. Progressive additions of cutter would result finally in attainment of a maximum point **C**, which can be observed also in the actual examples shown in Figures 4 and 5. Further additions result in a decrease in observed heater coating due to the fact that rapid settling takes place (**CD** and **DE**) finally reaching zero heater deposits at **E**.

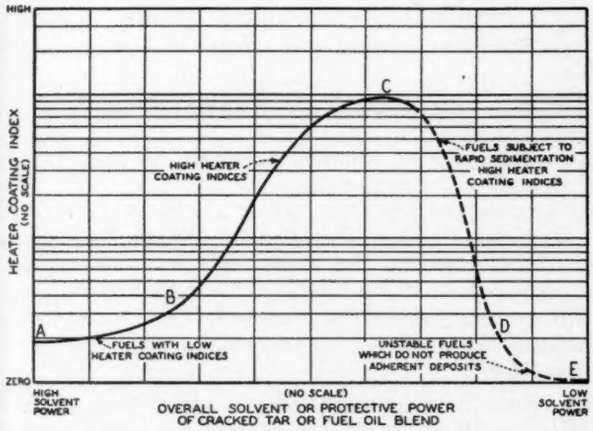


FIGURE 6

Heater-Coating Characteristics of Fuels as a Function of Solvent Power.

Most cracked fuels blended with cracked gas oil or other satisfactory cutter would be represented by the region **A-B**. Region **B-C** represents fuels which have either high benzol-insoluble contents and only moderate solvent power, or low benzol-insoluble contents and low solvent power. When two fuels from anywhere in the range **A-B-C** are blended, the heater-coating tendency of the blend will be intermediate or lower than either. Fuels shown at **C-D** and **D-E** have extremely poor solvent power, and may be expected to be unstable in storage. Their blending characteristics are like those of paraffinic cutter stocks. It is of interest to note that addition of aromatic cutters, or of asphalt to fuels represented at **C-D**, usually results first in an increase in the heater-coating tendency (due to prevention of sedimentation) along path **D-C** and then in a lowering along path **C-B-A.**

Lightly cracked paraffinic stocks may be represented along **C-D-E.** As cracking is usually carried out, cracked tars from any source are found at **A-B** and sometimes **B-C.**. Mixed fuels which might be shown along **B-C** or **C-E** may be obtained in ships' bunkers through mixing of cracked fuels and paraffinic straight-run fuels, each of which might be satisfactory prior to mixing.

Wherever an increase in heater-coating characteristics is due solely to an increase in the content of benzol-insoluble material, as for instance by more severe cracking of a given crude, there is a consistent relationship between heater-coating index and the usual sediment tests (percent benzol insoluble, B. S. and W., and sediment by extraction). Changes in heater-coating index in the region **A-B-C** (Figure 6), and especially along **A-B**, where due to the use of different type cutters, or to the addition of protective agents, are either inadequately or imperceptibly reflected in the B. S and W. and sediment-by-extraction tests. Additions to a fuel which might be represented along **A-B**, of sufficient cutter to bring it beyond the point **C**, generally results in a sharp increase in B. S. and W. and sediment by extraction. The fundamental weakness of tests which involve dilution with benzol or the like lies in the fact that the preponderant number of diluent molecules serves partly to obscure important differences between any solvent or protective action which may be exerted by the oil and asphaltic content of fuels; the response of such tests to serious instability (**C** or **CD**) is due to the inability of even benzol to re-disperse carboids once their original strongly-protective structure is broken. This latter, incidentally, suggests the advisability of making blends under conditions which avoid excessive local concentrations of cutter stock, and that increased temperature confers some advantage in blending because of the increase in solvent power.

Of all the fuels so far examined, no appreciable sedimentation of hydrocarbon material has been observed in fuels which might be represented along **AB.** In the region **BC** the sedimentation rate is seldom serious; and, when due to excessive dilution or to the use of paraffinic cutter with a given cracked tar, will be found to be roughly proportional to the heater-coating index.

CONCLUSIONS

The results of heater tests indicate the following:

1. Whereas the decrease in API gravity incident to

deeper cracking may properly be considered as a measure of the degradation of a stock with respect to the possibility of further cracking, it has no such connotation insofar as fuel-oil quality is concerned. Indeed, low gravity is indicative of high solvent power and, therefore, of a high degree of compatibility with cutter stocks and with other cracked fuels.

2. Although the benzol-insoluble content is to some extent a measure of the heater-coating potentialities of a fuel, the rate of deposition is so dependent upon the solvent or protective action of the other constituents that its presence means little more than that coating is a possibility. The same reasoning applies to sediment by extraction and sediment removal by super-centrifuge.

3. Cracked fuels with satisfactory heater-coating and stability characteristics can, as far as is known, be safely blended with one another. The effect of additions of straight-run fuels from asphalt-bearing crudes depends upon the relationship between the protective action of the asphaltic constituents and any precipitating tendency the light-oil portion may have, and cannot be predicted from the usual tests.

Because straight-run fuels deposit no hydrocarbon material, the heater deposit can be used as a research tool to measure the effective degradation caused by the combination of cracking and blending. The results are meaningless whenever the cracked fuel has been so severely diluted with low-solvent-power stock. that precipitation takes place within a short time. Under proper conditions the heater test can be used to determine both cracked-tar quality and the blending characteristics of straight-run fuels.

Correlation with tests carried out over a considerable period with a limited number of fuels from related stocks indicates that scaling off of heater deposits occurs at about the same time for fuels with both high and low indices. The net effect is that the heater surfaces are rapidly coated by a thick layer of carbonaceous material when fuels with high heater-coating indices are used, while with fuels of reasonably low heater-coating index scaling begins before a heavy deposit has had time to form.

It is believed that the use of fuels of any gravity which contain suspended carbonaceous material or undissolved heavy asphaltenes will be found to result in the formation of more soot and stack solids than would be obtained under the same conditions with a stable fuel.

APPENDIX

Description of Apparatus and Procedure

The heaters consist of tubes, 0.700 inches in diameter, heated by steam and immersed 8½ inches in approximately one quart of oil contained in a vessel, which is itself immersed in a water bath at approximately room temperature. Six heaters are mounted on a steel bench, 66 inches long, 12 inches wide, and approximately 24 inches high.

Steam pressure is kept at 135 pounds gage. To avoid excessive pressure drop through the heaters, no more than three heaters should be connected between the steam line and the trap. In order to insure effective working of the trap, allow 4 feet to 6 feet of bare piping between the trap and the nearest heater. High-pressure steam should be reduced to 135 pounds, using a reduction valve protected by a relief valve, with provision made for removing any super-heat.

The construction and mounting of the heaters are illustrated in Figures 7 and 8.

OPERATION

Before being charged the heater surface is polished with a naphtha-base metal polish and wiped with a clean cloth. The cylindrical oil container is then filled to such a height that the heater surface is immersed 8 inches to 8½ inches and screwed into place. The water baths are then mounted, filled, and the steam turned on. The temperature of the water bath is not critical, but should be kept from 60° to 80°F.

The oil is changed each 24 hours, and the deposit removed after 96 hours. To minimize oxidation reactions, the steam pressure should be relieved 15 minutes before removing water baths or oil containers. The water baths are removed, the oil containers taken off, and the tubes drained for approximately 30 minutes. During this time the oil containers can be re-filled.

It is important that inlet-steam valves be tight so that the heater tubes can be cooled as above.

The fuel is changed by pouring out of the container and re-filling. After the completion of the four-day test the containers are cleaned out, using kerosene or mineral spirits, and dried before re-charging with another fuel. The container should be free from water in order to prevent foaming. Failure to remove thinner used in cleaning will affect the heater-coating index.

REMOVAL OF DEPOSITS

Tubes should be allowed to drain 30 minutes before deposits are removed.

Erratic deposition takes place at the surface of the oil. For this reason the deposit above 7½ inches from the bottom of the tube, and on the bottom, is first removed—a cloth slightly moistened with benzol or chloroform facilitates removal. The 7½-inch line is marked by a slight projection on the wall of the heater tube.

The deposit to be weighed is washed into a beaker containing 30 cc. to 40 cc. of benzol, using a small semi-circular brush with stiff bristles which is frequently dipped into the benzol. Repeat with an equal quantity of benzol. Pour all washings into a 100-cc. stoppered graduate, and make up to 100 cc. with benzol. This last addition may be used to remove thoroughly any adhering deposit from the brush. Shake well, and allow to stand two hours before filtration onto a tarred asbestos Gooch crucible. In the case of heavy deposits, the filtration can be speeded by decanting most of the benzol-oil solution onto the filter before stirring up the benzol-insoluble material. Approximately 50 cc. of fresh benzol should be used for washing the deposit and the sides of the

crucible. The washings should be clean. Dry under the same conditions used in preparation of the tarred Gooch, and weigh. The weight, expressed in grams, is termed the "heater-coating index."

PREPARATION OF CRUCIBLES

Tight filters which do not lose fiber can be prepared by sucking a water suspension of coarse prepared asbestos onto a Gooch crucible, tamping, and following with a tamped and finally an untamped layer of fine asbestos; the suction should be relieved when adding the suspension. The first, as well as the subsequent layers, should be free from holes. A.S.T.M. "standard specification bitumen" crucibles have been found to be very satisfactory for the purpose.

The degree of coarseness of the suspended asbestos is governed by the time of stirring. The coarse suspension may be made as follows:

Add 60 grams of coarse prepared asbestos to 4 liters of water in a balloon flask, heat to 120-150°F., and stir vigorously for 10 minutes, using a paddle turned by a stirring motor. The suspension of fine asbestos can be made by adding one liter of the coarse suspension to two liters of water, and stirring for 30 minutes as before.

Crucibles should be dried in an oven and stored over calcium chloride in a desiccator. Drying in the preparation of the crucibles and, after use, can be

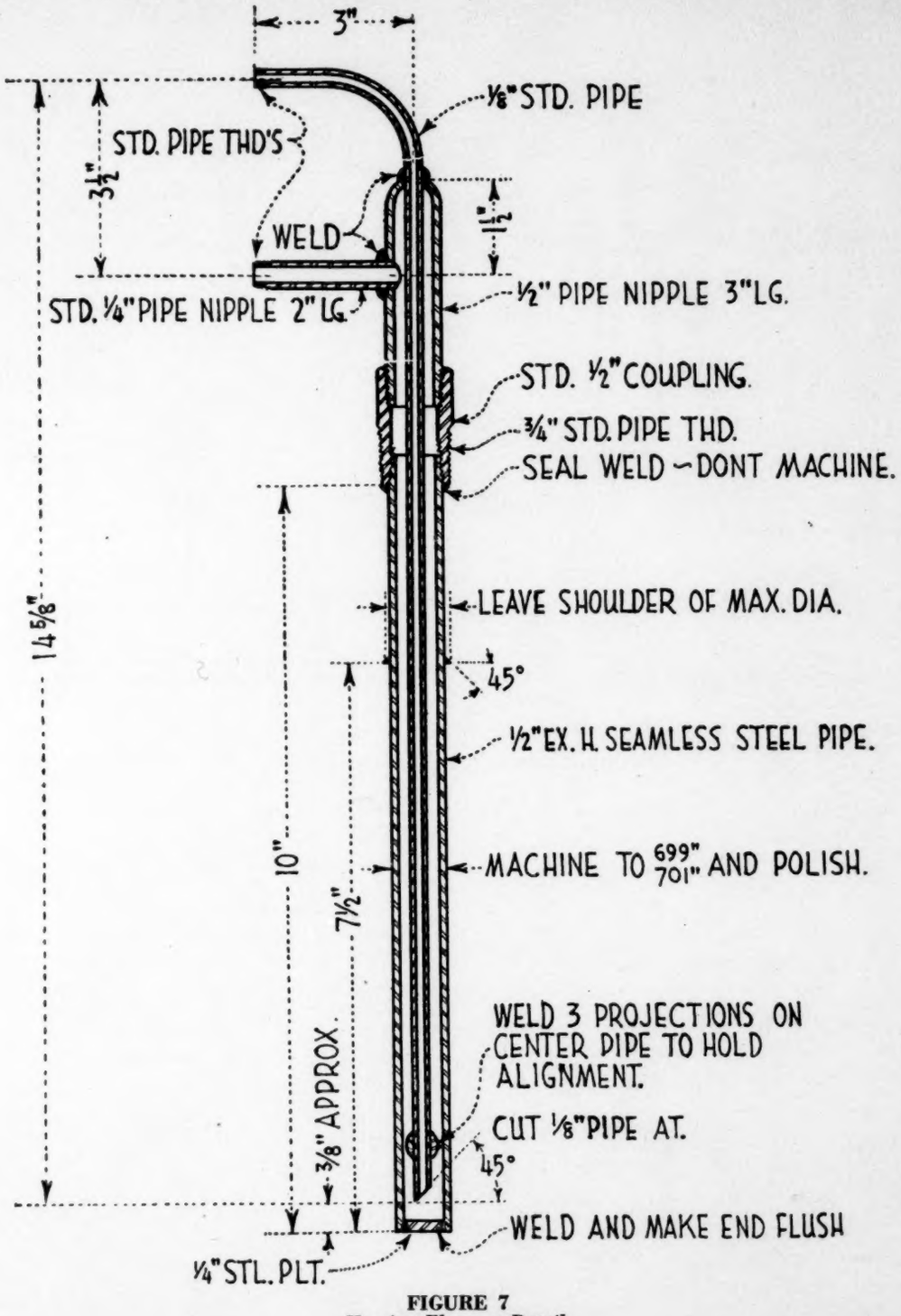


FIGURE 7
Heating-Element Detail.

carried out rapidly in a steam oven at not over 200° F. or in a heated vacuum desiccator.

DETERMINATION OF BENZOL-INSOLUBLE CONTENT

Weigh 8 to 10 grams of tar or fuel accurately into a 100-cc. stoppered graduate. Add 10 times as many cc. of benzol, to the nearest cc., as there are grams of sample, and shake until homogeneous. Allow to stand at least two hours, and filter onto an asbestos Gooch as described for determination of heater deposits.

This method is an adaptation of the "revised method of determining sediment in fuel oil," described by R. R. Curley (Lieut. U.S.N.) and J. G. O'Niell, *Journal of the American Society of Naval Engineers*, May, 1934.

QUALITY OF BENZOL

Because of its content of high-boiling fractions, the so-called 90-percent benzol has been found to be unsatisfactory for this use. Commercial 100-percent water-white benzol, boiling range 80-82° C., has been found to be as satisfactory as C.P. benzene.

HAZARDS DUE TO USE OF BENZOL

It should be kept in mind that benzol vapors are toxic. Personnel should be instructed to avoid contact with the liquid or spillage upon clothing. Washing of deposits should not be carried out until the heater tubes are cool, and adequate ventilation should be assured.

Because of the great variability in individual susceptibilities, and to the sometimes vague nature of the symptoms of benzol poisoning, it is best that precautions be taken completely to remove the possibility of injury from this source. The use of the lighter type of respirator, commonly used in paint spraying, was found to offer adequate protection during the washing of deposits. Filtration of heater deposits and benzol-insoluble contents should be carried out in a hood equipped with forced draught.

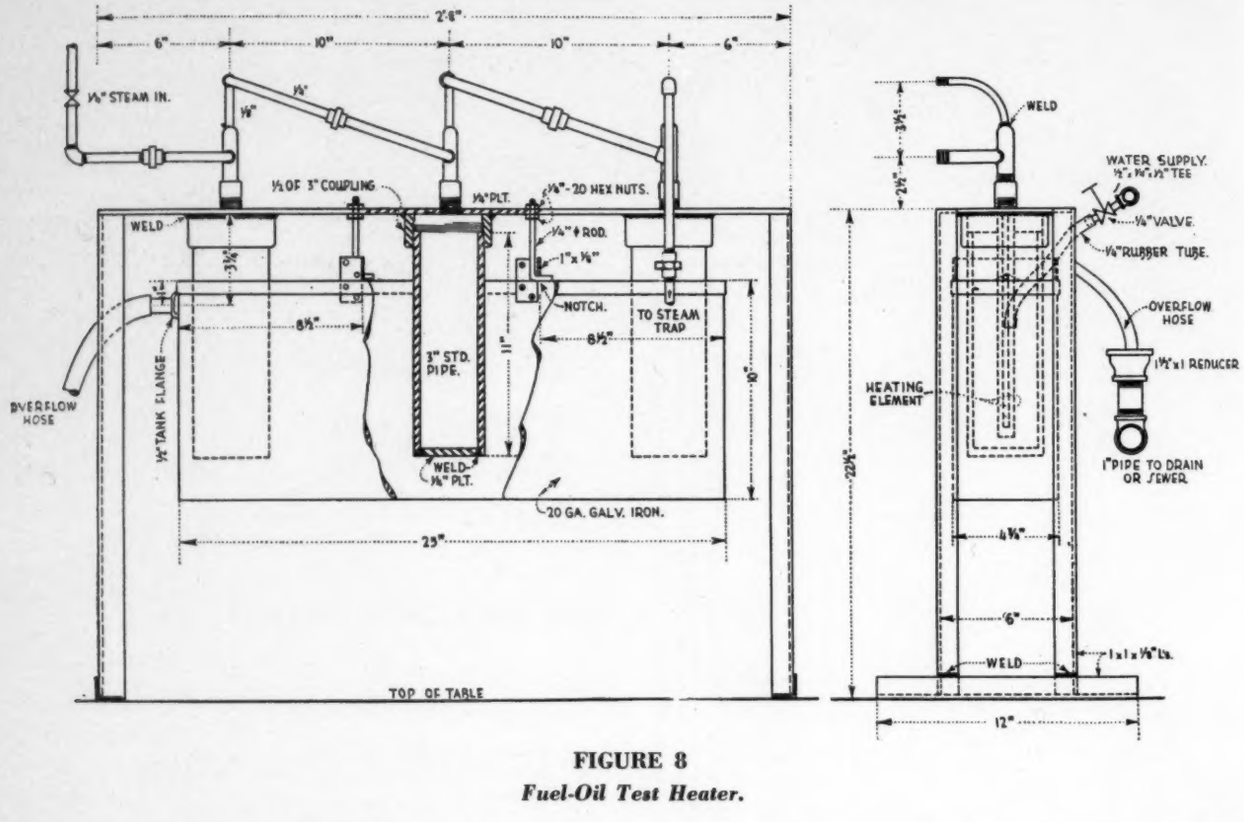


FIGURE 8

Fuel-Oil Test Heater.

The Newer Bearing Materials and Their Lubrication

H. G. MOUGEY

H. C. MOUGEY, *of General Motors Corporation, Detroit, Michigan, read the accompanying paper at the Division of Refining group session Thursday morning, November 12, in connection with the American Petroleum Institute's Seventeenth Annual Meeting at Chicago, Illinois.*

Mr. Mougey was graduated in chemistry by Ohio State University in 1911. Until 1917 he was research chemist for a paint and varnish company. He entered the employe of General Motors Corporation during this same year in the research laboratories section and has continued as its chief chemist. His work has been diversified, his main interests being automobile finishing, plating, and lubrication.

INTRODUCTION

THE subject of bearings covers a very large field. Whenever two surfaces rub together, we have a bearing. As an illustration of a thrust bearing we may cite the block or device that applies pressure on one end of a rotating drill to cause the other end of the drill to make a hole. Long before mankind had developed from the state of savages, the drill with thrust bearing was in common use to produce holes in shells, beads, etc. We are all familiar with the sliding bearing, such as when a piston slides in a cylinder. We are also familiar with the rotating bearing, such as we have when a journal rotates in a bushing or when a wheel turns on an axle. In this discussion we shall confine ourselves to this last type of bearing, the rotating bearing such as we have at the center of a wheel.

Now it is evident that in order to have a bearing at the center of a wheel, we must first have a wheel. The wheel is very old, and we do not ordinarily give much thought to the invention of the wheel; but, in reality, the wheel is a very complex structure, and it required a very high order of invention to produce the wheel.

When Columbus discovered America the North American Indian was in the Stone Age, and the wheel was unknown. In Mexico and Yucatan the inhabitants had progressed further on the road toward civilization, but they were still in the Stone Age. It is true that they built many fine paved roads, temples, pyramids, etc. They knew considerable about astronomy, agriculture, mining, architecture, and even metallurgy; but they did not know about the wheel. In South America the Incas of Peru had developed even further. They were in the early Bronze Age, and made alloys of copper and tin; they had many hundreds of miles of wonderfully paved roads; they had domesticated the llama to carry burdens—but they had no wheel. There were no oxen nor horses in the entire new world to pull a cart or wagon, even if the wheel had been invented.

The beginning of civilization dates back many centuries, but the earlist recorded date in the whole world is 4241 B. C., which marks the invention of the calendar by the Egyptians. The Egyptians divided the year into 12 months of 30 days each with 5 holidays to make up the 365 days. This calendar, with a few slight modifications, is the one which is now in use in practically the whole world. However, it was not until more than 1,000 years after the Egyptians had invented the calendar that they reached the state of civilization when they built the pyramids; and it was not until more than 1,000 years after the building of the pyramids that the Egyptians knew about horses and wheels.

By the time of the Greeks and Romans the chariot had become more or less obsolete as a major instrument of war; but for many centuries it kept its place as a means of transportation. However, there was very little fundamental difference between the wheels and bearing requirements of the early chariots and those of horse-drawn vehicles as late as the time of George Washington; and, as a result, there was little incentive to develop or improve bearings during this entire period of time, which amounts to about 4,000 years.

The first commercial steam engines—which, during the period of from 1705 to 1780, were used largely for pumping water—were very crude affairs, and their bearing requirements were not severe. However, the improvements by Watt, dating from 1769, soon developed the steam engine to a state where better bearings were required for both engines and the machines operated by the engines. As a result of this need, attention has been focused on this problem, and within the last 100 years many developments have occurred.

BABBITT PATENT

The first of these inventions, and probably the most important, was that of Isaac Babbitt, Patent No. 1,252, July 17, 1839. This invention consisted in lining a metal shell with an alloy of the general type of pewter. Ever since the time of this invention, an alloy of the general composition of pewter, when used for bearing purposes, has been known as "babbitt." Contrary to the commonly accepted idea, Babbitt did not invent the alloy which bears his name; and, as a matter of fact, tin-base alloys similar in composition to the kind of material used by Babbitt in this bearing had been known for thousands of years. The

following quotations and the sketch (Figure 1) from Babbitt's patent show that Babbitt simply used pewter or Britannia metal or some similar alloy already

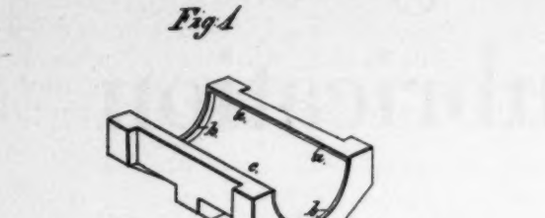


FIGURE 1

well known,, and the chemical composition of the pewter was not the important part of the invention:

Lines 22 to 31 (Patent No. 1,252):

"The inner parts of the boxes are to be lined with any of the harder kinds of composition known under the names Britannia metal or pewter, of which block tin is the basis. An excellent compound for this purpose I have prepared by taking about 50 parts of tin, five of antimony, and one of copper, but I do not intend to confine myself to this particular composition."

Claim, lines 93 to 101 (Patent No. 1,252):

"The making of the boxes for axles and gudgeons, in the manner above set forth; that is to say, by the casting of hard pewter, or composition metal, of which tin is the basis, into said boxes, they being first prepared and provided or not with rims or ledges, and coated with tin, as herein described and made known.

ISAAC BABBITT."

Since Babbitt's time many people have worked on the subject of bearings, and as a result there are now a number of bearings of different types. Some of the most important of these bearings, together with their composition and the date of their invention, are as shown in Table 1.

WHAT IS A BEARING?

There is certainly a very wide range of materials and percentages of these materials in this list of bearings and, consequently, it may be desirable to raise the question: "what is a bearing?" There are two theories that have been advanced to explain bearings. According to one theory a bearing must be a combination of hard crystals in a matrix of softer material; the hard crystals are supposed to carry the load, and the softer matrix is supposed to permit deformation of the bearing so as to permit a more nearly uniform distribution of pressure.

It is our belief that the "hard crystal and soft matrix" theory is incorrect, and that this theory has very greatly retarded the development of bearings. It is true that certain soft metals, such as lead, tin, cadmium, etc., although good in anti-friction and anti-scoring properties, are low in mechanical strength and an increase in mechanical strength may be obtained either by bonding these materials in thin layers to stronger materials or by combining them with certain materials to give a fine mechanical mixture of soft metal and hard crystals. However, it is the resulting combination of properties, and not the hard and soft crystal method of obtaining these properties, that is important.

TABLE 1

Some Bearings and Their Composition

BRONZES (OR HIGH COPPER ALLOY)

	Copper	Lead	Tin
1870—Dick	80	10	10
1892—Dudley	77	15	8
1900—Clamer and Hendrickson (73)		20 (minimum)	7 (maximum)

1904—Clamer (Patent No. 769,337). A stiff back with a lining of high melting point. (This is the original steel-back copper-lead bearing.)

HIGH LEAD ALLOYS

1905—"No Heet"	Lead	96-99.5
	Sodium	4- 0.5

1915—Ulco metal, Frary metal, Mathesius, Lurgi Lagermetall, Bahumetal, Satco etc. (lead hardened with alkali and alkali-earth metals).

CADMIUM ALLOYS

1909—Touceda, Patent No. 934,637	Cadimum	95-99.5
	Magnesium	5- 0.5
1933—Schwartz and Phillips, Patent No. 1,904,175.....	Cadmium	93-99.75
	Nickel	7- 0.25
1935—Smart, British Patent No. 436,633	Cadmium	97.0-98.0
	Copper or Nickel	0.25- 0.50
	Silver	1.75- 2.50

SAE BABBITTS (TYPICAL COMPOSITIONS) (ADOPTED 1922)

SAE No.	Tin	Lead	Copper	Antimony
10	90.0	0.35 (maximum)	4.5	4.5
11	87.0	0.35 (maximum)	5.75	6.75
12	59.50	26.00	3.0	10.50
13	5.0	84.0	0.50 (maximum)	10.0
14	10.0	74.0	0.50 (maximum)	15.0

SPECIAL COMPOSITIONS

Graphite bearing metal, oilless bearings, porous bearings, Graphalloy, Genelite, Durex, Oilite, etc. (porous bearings, high in copper, and containing small amounts of such materials as tin, lead, graphite, etc. These bearings are usually impregnated with oil before use.)

According to the second theory the crystal structure is of little or no importance, but the bearing must have a combination of properties so that it will resist the forces to which it may be subjected in service. These properties are tabulated in Table 2.

TABLE 2

Bearing Properties

1. Mechanical strength
2. Bonding characteristics
3. Melting point
4. Fatigue resistance
5. Anti-friction characteristics
6. Non-scoring characteristics
7. Corformability
8. Embeddability
9. Corrosion resistance

The particular combination of properties required by a bearing depends upon the forces to which the bearing is subjected. Leaded bronze, of the composition copper 88, tin 4, lead 4, and zinc 4, is excellent

for the bearing for the small end of an automobile connecting rod; and steel-backed, high-tin-base babbitt bearings are in general use for the large ends of connecting rods—but very unsatisfactory results would be obtained if these bearings were reversed, and the leaded bronze of the above composition used for the big end and the babbitt for the small end.

A cake of paraffin is excellent in properties 5, 6, 7, 8, and 9 in the table of "bearing properties," but it would make a poor connecting-rod bearing on account of being very poor in properties 1, 2, 3, and 4.

Under certain conditions other properties or combinations of properties may be important. Canvas impregnated with bakelite is coming into general use for certain very severe bearing conditions, such as some of the bearings in steel mills; but this material is unsatisfactory for automobile connecting-rod bearings for high-speed operation, because the heat generated at the bearing surface cannot be dissipated rapidly enough, and the rubbing surface of the bearing soon chars.

In general, a bearing metal need not have all of the properties in Table 2; it requires only the ones that will enable it to resist the forces to which it will be subjected in service. Tin-base babbitt (SAE 11) is in general use in large-end connecting-rod bearings; but SAE 11 is very low in mechanical strength, in melting point, and in fatigue resistance. However, it is excellent in its bounding characteristics, and the combination of a steel back bonded to a very thin lining of SAE 11 produces a bearing which is much superior to a straight SAE 11 bearing in mechanical strength and fatigue resistance. The anti-friction characteristics of a steelback babbitt-lined bearing are so good that the temperature rise due to friction may be low enough so that the low melting point of the SAE 11 is not fatal. Such a bearing is good in non-scoring characteristics, in conformability, in embeddability, and in corrosion resistance.

However, most tin-base and lead-base babbitts tend to lose their strength very rapidly at elevated temperatures.[2] This tendency is shown by the curves in Figure 2. In modern automobile engines this loss in strength, due to higher crankcase temperatures, is so

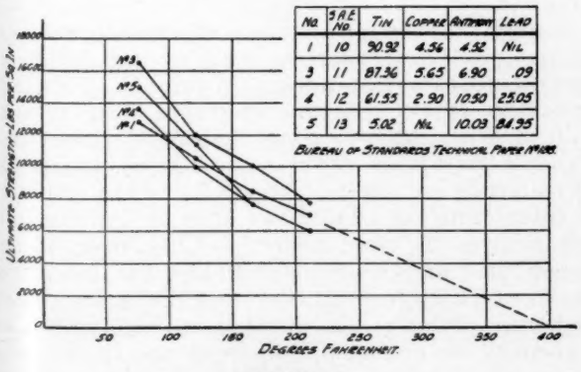

No. | SAE No. | Tin | Copper | Antimony | Lead
1 | 10 | 90.92 | 4.56 | 4.52 | Nil
3 | 11 | 87.36 | 5.65 | 6.90 | .09
4 | 12 | 61.55 | 2.90 | 10.50 | 25.05
5 | 13 | 5.02 | Nil | 10.03 | 84.95
Bureau of Standards Technical Paper #188
Ultimate Strength - Lbs. per Sq. In.
Degrees Fahrenheit
50
100
150
200
250
300
350
400

FIGURE 2

serious that many attempts are being made to replace SAE 11 with other materials. In the case of connecting rods for airplane engines, SAE 11 is already practically obsolete, and other bearing materials that have higher strength at elevated temperatures are in general use. Lead and cadmium have higher melting points than tin; and, although these metals do not offer as much increase in strength at elevated temperatures as might be desired, they may have enough advantage over tin—especially in borderline cases—to make all the difference between success and failure. High-lead-base bearings and cadmium bearings are coming into general use for such types of service as connecting rods for diesel engines.

In trying to replace SAE 11 it is ery easy to get a material that will be superior in one or two respects, such as mechanical strength or high melting point; but such a bearing may be lacking in other important respects, such as corrosion resistance or anti-friction characteristics or non-scoring characteristics. When used in crankcases with corrosive oils or with oils that become corrosive due to oxidation of the oils, certain high-lead or cadmium bearings may fail very rapidly due to corrosion. Attention has previously been called to the fact that the alloy,-copper 88, tin 4, lead 4, and zinc 4, is unsuitable for large-end connecting-rod bearings in automobile engines. This is because it will cause scoring of the crankshaft under hign-speed operating conditions, although it will not score the shaft under sufficiently low-speed operating conditions. It is due to the low rubbing speed at the small end of the connecting rod that this alloy can be used for a piston-pin bearing.

SCORING

This problem of non-scoring is one of the most important in developing connecting-rod bearings; but, unfortunately, we have very little reliable information as to why certain metals score and others do not. In discussing this general problem Tomlinson[3] says:

> "It is not easy to obtain any direct experimental evidence that molecular cohesion takes place, although strong molecular forces would be expected when the boundaries of two solids are brought together within the range of the molecular fields. That molecular cohesion occurs when two clean solids touch seems to be certain. Sir W. Hardy has expressed the opinion that the static friction between clean surfaces is due to cohesion."

Bowden and Ridler[4] have reported in the *Proceedings of the Royal Society* on some work that they did to determine the temperatures of the surface layers of bodies during sliding. The surface temperature was measured by using the rubbing contact of two different metals as a thermocouple, and determining the electromotive force generated on sliding. Experiments showed that the local temperature—which depended upon load, speed, coefficient of friction, and thermal conductivity—might be surprisingly high, reaching more than 1,000° C. (1,832° F.) in some cases. With lower-melting-point metals, the melting point of the metal was the maximum temperature that could be reached. In tests on lubricated surfaces they obtained similar results. For example, a polished metal surface, well lubricated with "Castrol XL," and running smoothly with a low coefficient of friction, showed a surface temperature of over 600° C. (1,112° F.). This high temperature was localized at the sliding surface, the mass of the metal was at room temperature, and there was no evident sign of heating.

A joint research committee of the American Society for Testing Materials and the American Society of Mechanical Engineers has been working on the "Effect of Temperature on the Properties of Metals." In this work the seizure of metals at elevated temperatures has been studied. The following sentences are taken from a condensed report of this committee.[5]

> "One of the causes of failure of metals at high temperature is seizure, the incipient welding together of

two metal surfaces in contact. . . . While perfectly matching surfaces will weld readily, in order to bring surfaces of ordinary smoothness of finish into molecular contact it is usually necessary that one surface at least be fairly plastic and be pressed against the other so as to force them into molecular contact. In many such cases plasticity is brought about by elevated temperature, so that the seizure problem is quite generally a high-temperature problem. . . . Unless they are soluble in the solid metal at the temperature in question, oxide and other non-metallic films prevent metallic contact of the coating surfaces, and may thus prevent seizure. A film of oil, or even of adsorbed gas, will likewise prevent contact."

The findings of this committee are in accord with the results of work at the National Bureau of Stand-

Of course, under true "fluid-film" lubrication conditions, there is a film of oil between the metal surfaces—and scoring is prevented by this film of oil, and the composition of the bearing metals is of no importance. However, when this fluid film breaks down, then it appears to be necessary that the bearing metals must be separated by a film of some kind to prevent molecular contact with resulting scoring or welding. In the case of "extreme-pressure" lubricants, which are attracting so much attention at the present time on account of their importance for the lubrication of hypoid gears, the film which prevents scoring is iron sulfide or iron chloride or some simi-

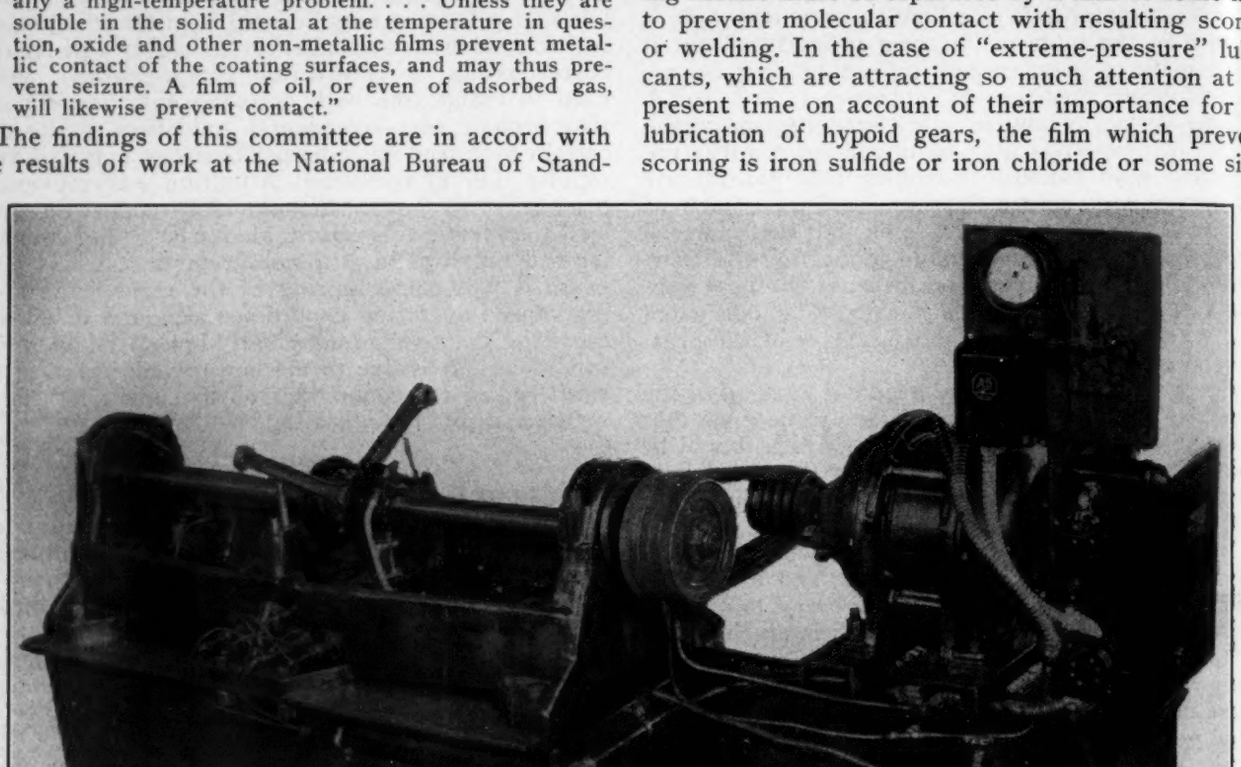


FIGURE 3

ards,[6] in which it was found that under certain conditions of load and rubbing speed, with steels of certain properties, metal-to-metal contact would occur, and that seizing, welding, and very rapid wear would occur. However, if the test conditions were modified somewhat, adherent oxide films would form on the surfaces of the steel; and, under exactly the same conditions of load and rubbing speed, these oxide films would prevent metal-to-metal contact; and, as a result, there would be no signs of seizing or welding, and the rate of wear would be extremely low.

In the report of the joint ASTM-ASME committee[5] descriptions are given of various testing machines which are used to determine the non-scoring characteristics of metals, but experience indicates that it is difficult to obtain check results with such machines unless all the test conditions are very carefully standardized; and it is difficult to correlate the results of such machines with performance in service. For this reason a test in an engine under actual service conditions is the only true test of non-scoring; and, since the requirements in different engines may be different, a bearing that scores in one engine may be non-scoring in another engine of slightly different design or operated under different conditions.

lar material. In the case of tin, lead, or cadmium bearings as used in connecting rods in automobile engines, it appears that a film of some kind must be formed so easily with all oils that scoring is not a problem with these bearing materials. Under non-corrosive conditions, failures of these types of bearing materials are due to "fatigue," and the quality of the lubricating oil usually has little or nothing to do with failures of these bearings. Of course, it may happen that under some conditions the lubricating system of an engine cannot keep the bearings supplied with oil due to the oil being too high or too low in viscosity, or due to the oil being too far below its pour point— and in such cases the bearings may fail due to lack of oil of any kind, regardless of the quality of the oil.

FATIGUE RESISTANCE

Since with clean oil and in the absence of corrosion or scoring troubles, bearings fail by lack of resistance to fatigue, and since resistance to fatigue in an engine cannot be determined by the conventional tension, compression, or impact tests, and since the quality of the oil usually has little or nothing to do with resistance to fatigue, it is very important in developing

bearings to be able to measure resistance to fatigue. This can be done by operating the bearings in an engine under very high-speed, high-temperature, and high-load conditions. This actual engine test must always be made as the final test before drawing definite conclusions as to resistance to fatigue. However, under these severe conditions, other parts of an automobile engine are also subject to failure, and it is not a simple matter to make fatigue tests in engines. Consequently, for preliminary work, a laboratory testing machine is desirable.

The loading on connecting rods is quite different from the loading on bearings used for line shafts, etc. In the case of a connecting-rod bearing the load travels around the inside of the bearing; and, on account of the lightness of the connecting rods, a certain amount of deflection of the bearings usually occurs. In our laboratory we use a bearing testing machine like the one shown in Figure 3 and Figure 4. The eccentric weights (**A-A**) tend to make the shaft "bow out," thus putting a rotating load on the inside of the connecting-rod bearings (**B-B**). The connecting rods are spaced at an angle of 90 deg., and are held with piston pins at the small ends (**C-C**). The eccentric weights (**D-D**) are for the purpose of counterbalancing the weights (**A-A**), so that the testing machine as a whole does not vibrate. Oil is fed to the bearings under test by holes in the shaft (**E**), so that the bearings are lubricated just as they would be in an engine.

The temperature of the oil is controlled by electric heaters immersed in the sump. The temperature of the bearings is determined by thermocouples embedded just beneath the surface of the babbitt, and the temperature of the oil in the sump is controlled so as to maintain the bearings at the predetermined temperature. In our work this bearing temperature is usually 174° C.-176° C. (345°-349° F.). The temperature of the oil in the sump is usually between 135° C. (275° F.) and 149° C. (300° F.) since the difference in temperature between the oil in the sump and the bearing depends upon such factors as load speed, bearing clearance, oil viscosity, coefficient of friction of the bearing, etc. The test machine is usually operated at a speed of 4,500 r.p.m., with the eccentric weights adjusted to give a calculated bearing load of 1,400 lb. per sq. in. projected area. If the bearings are not resistant to corrosion, the test must be made with an oil that will not develop corrosive acids on oxidation under the test conditions. If it is desired to test the performance of the bearings with corrosive oils, then either 1 per cent of oleic acid is added to the lubricating oil, or corrosive acids are allowed to form as the result of oxidation of the oil in the test machine. In our tests we have standardized on SAE 30 oil, although we do not find any measurable difference in bearing life in engines over the range of viscosities of from 10-W to SAE 40, provided the lubricating system in the engine can keep the bearings supplied with oil under all conditions.

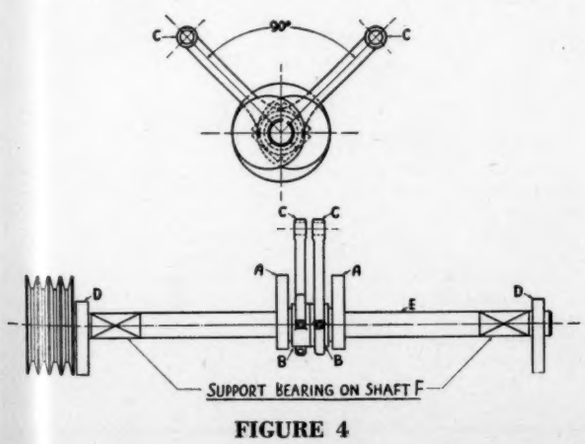


FIGURE 4

By means of this machine it is possible to compare the fatigue resistance of different bearing materials, making the tests in the actual connecting rods in which the bearing material is to be used. Since the details of construction of the rod and of the bearing greatly affect the resistance to fatigue, an inferior bearing material in a well-designed rod may be superior to a better bearing material in an inferior rod. For this reason it is impossible to give definite figures as to the relative merits of different bearing materials, and each engineer tries to get the best all around results in his own engine.

COMFORMABILITY, EMBEDDABILITY, CORROSION RESISTANCE

Conformability is the property of a bearing that permits it to deflect or distort enough to give a more uniform distribution of pressure. This result may be accomplished by design of the bearing or by composition of the bearing alloy, or both. The cap of an automobile connecting rod is subject to much higher calculated loads than the part of the bearing in the main part of the rod; but due to the fact that the cap is usually sufficiently flexible to permit a more uniform distribution of the load, the life of the cap half of the bearing is usually much greater than that of the rod half of the bearing.

Embeddability is the property of the bearing that permits the embedding of small particles of dirt in the bearing, thus decreasing the abrasive action of these small particles. Examination of a used babbitt bearing will usually show many small particles of iron, or other hard materials; but these have been embedded in the bearing to such an extent that they no longer tend to cause abrasion.

Corrosion resistance is a property that may be very important. Ordinary mineral oil, regardless of the crude or method of refining, is usually very low in acidity or corrosive tendencies. However, under certain conditions, as the result of oxidation—especially at elevated temperatures—organic acids that probably are quite similar to oleic acid may be formed. Lubricating oils differ greatly in their tendency to form acids by oxidation under high-temperature conditions. All crudes contain varying amounts of inhibitors that decrease the tendency of oils to oxidize, but these inhibitors may be removed from the oil to a greater or less extent by the various refining methods. As a result, a year or so ago, many of the more highly refined lubricating oils were subject to oxidation at high crankcase-oil temperatures, with the resulting development of acids that would corrode certain bearing materials such as cadmium or some of the high-lead materials. This subject is getting to be better understood by oil chemists and, as a result, many oil companies are now in production on lubricating oils that, although very highly refined, are very resistant to the development of corrosive acids.

It is evident that there are three solutions to the

problem of corrosion of bearings. These solutions are:

1. Develop oils that will not form corrosive acids, even under severe operating conditions.
2. Decrease the crankcase temperatures to such an extent that all oils will be free from oxidation.
3. Use bearings that are not subject to corrosion, even with acid oils.

CONCLUSION

From the standpoint of the bearings, much progress is being made. The high-tin babbitts, SAE 10, 11, and 12, and the high-lead babbitts, SAE 13 and 14, are not subject to corrosion in engines. Cadmium bearings, of present composition, are subject to corrosion, as are also certain of the high-lead babbitts such as those hardened with alkali and alkaline-earth metals. Copper-lead bearings are a sponge of copper holding practically pure lead in the pores of the copper sponge. Corrosive acids remove the lead from the surface of such a bearing, leaving a bearing surface of copper but without the increase in clearance that would result from the corrosion of cadmium or high-lead bearings. Under present conditions it is easy for an automobile company to change in production from one bearing material to another. Consequently, bearing materials now in production may not be the same as those that will be used six months from now. Probably all the bearing materials now in use will continue to be used, wherever they are found to be suitable, and the probabilities are that the list of bearing materials will be increased as a result of a better knowledge of the entire bearing problem.

This problem of lubricants for the newer bearing materials, which at first appeared to be rather serious, is now being handled in a very satisfactory manner. The oil and automotive engineers have cooperated on this problem; the oil engineers have made improvements in their lubricants, and the automotive engineers have done what they could from the standpoint of the engine and the bearings. From time to time in the past, situations have arisen which at first appeared to be very serious. However, as the result of cooperation between the oil and automotive engineers, these problems have been solved. The list of these problems includes such subjects as those shown in Table 3.

TABLE 3

Problems Solved by Cooperation Between the Petroleum and Automotive Industries

1. Crankcase dilution
2. Crankcase corrosion
3. Gum and anti-knock
4. Vapor lock.
5. Cold starting
6. Lubricants for the new bearing materials.

In the early days, crankcase dilution and crankcase corrosion were very serious problems, but improvements in gasoline and the use of crankcase ventilators and jacket-water temperature control solved the problem. When gasolines of improved anti-knock properties were first made, considerable trouble due to gum was experienced. However, both the oil and automotive engineers made the necessary changes, and this problem of gum is now of minor importance. Vapor-lock difficulties have not entirely disappeared, but the control of vapor pressure of the fuel and improved fuel-handling systems have resulted in this trouble being under control. Several years ago cold starting was very serious, but more suitable lubricants, together with improvements in starting systems, have corrected this situation. In a similar manner, as a result of the cooperation between the two industries, the problem of lubricants for the newer bearing materials is no longer a serious problem. It appears that by a continuation of this cooperation these problems may be kept under control, and other problems which may arise in the future may be solved.

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The Chemical Constituents of Lubricating Oil

A. P. I. Research Project 6

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ABSTRACT

THE PROBLEM of the chemical constitution of the lubricant fraction of petroleum is discussed from the standpoint of providing fundamental data that will increase the economic utility of the material. The work of the Institute's Research Project 6 has yielded the following information concerning the constituents of a dewaxed, solvent-extracted, Mid-Continent petroleum: 1, the oil consists substantially of naphthene (cycloparaffin) hydrocarbons with from one to four rings per molecule, with paraffin side chains; 2, the oil contains no paraffin hydrocarbons. The possibility that present refining processes discard some desirable constituents is discussed.

This paper was presented at Seventeenth Annual Meeting, American Petroleum Institute, Chicago, November 12, 1936.

Publication approved by the director of the National Bureau of Standards of the U. S. Department of Commerce.

IN approaching the problem of the chemical constitution of the lubricant fraction of petroleum from the standpoint of providing fundamental data that will increase the economic utility of this material, as, for example, its use as lubricating oil, one may ask a series of questions:

1. What are the desirable properties of a lubricating oil?
2. How do the desirable physical and chemical properties change with the chemical constitution?
3. What are the constituents of the lubricating-oil fraction of petroleum?
4. What are the methods for separating the desirable constituents?
5. Do our present refining processes effectively separate the desirable from the undesirable constituents?

When available, the answers to these questions will comprise a solution to the problem of obtaining, from a given type of crude petroleum, the best constituents for use as lubricating oil.

It is possible at present to answer question (1) in the rather general terms of what a lubricating oil should and should not do in a given service, but the specific definition and evaluation of the several properties which combine to make an oil good for lubrication in a given service is the subject of intensive investigation in a number of laboratories at the present time. The answers to question (2) can be satisfactorily learned only by synthesizing appropriate compounds of known structure and subjecting these compounds (and known mixtures of them) to proper test and measurement. The answer to question (5) must be deduced from an analysis of given processes and their charging stocks and products.

The work of the Institute's Research Project 6 at the National Bureau of Standards is aimed to ascertain the answers to questions (3) and (4) above, i.e., to determine the chemical constitution of the lubricating-oil fraction of petroleum, in which work there must necessarily be developed methods and apparatus for effectively separating from each other: 1, the molecules of different size; 2, the molecules of different type; and 3, the isomeric constituents of similar size and type.

FREDERICK D. ROSSINI, *of National Bureau of Standards, United States Department of Commerce, Washington, delivered the accompanying report at the Division of Refining group session Thursday afternoon, November 12, in connection with the American Petroleum Institute's Seventeenth Annual Meeting at Chicago.*

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As chief of the section on thermochemistry and composition of petroleum, he has specialized in physical chemistry at the National Bureau of Standards since 1928. He is also director of A.P.I. Research Project 6; author of 28 scientific papers; co-author of a book on "The Thermochemistry of the Chemical Substances"; holds the Hillebrand Award for 1934 from the Chemical Society of Washington for researches on the thermochemistry of hydrocarbons and alcohols, and is a member of numerous scientific societies. He is a member, for the United States, on the Permanent International Commission for Thermochemistry of the International Union of Chemistry.

DESIRABLE PROPERTIES OF A LUBRICATING OIL

In order to be used efficiently in a given service, a lubricating oil should have certain properties which best fit it for that particular job. The desirable properties will, in general, vary with the work which the lubricant is called upon to do—although several of the requirements may be common to a number of services.

One may, for example, consider the properties which a lubricating oil should possess in order that it may render the best possible service in the functioning of the modern internal-combustion engine. The desirable properties have been enumerated by many writers; and,

while there is no general agreement, the questions most often asked concerning the merit of a motor oil are the following:

a. At the atmospheric temperatures likely to be encountered, will the oil be sufficiently fluid to permit reasonably easy starting of the engine?

b. At the temperatures and clearances occurring in the operating engine, will the oil provide an adequate film between the moving surfaces, i.e., have a proper viscosity, and, for severe operating conditions, have good "oiliness" characteristics?

c. Will the oil be reasonably stable under the conditions of operation, i.e., be adequately resistant to chemical reaction, such as oxidation, decomposition, or polymerization, at the operating temperature?

d. Will the oil be sufficiently non-volatile at the operating temperature to make the loss of it from this cause small?

e. Will the oil form hard carbon in the engine?

Several of these questions, such as those involving viscosity and volatility, are subject to evaluation by simple physical measurements; but others, such as those involving chemical stability and "oiliness," are much more difficult to evaluate.

The production of a lubricating oil of any desired characteristics involves the selection from the crude of the compounds having these characteristics.

EFFECT OF STRUCTURE UPON THE PHYSICAL AND CHEMICAL PROPERTIES OF PURE HYDROCARBONS

Examination of any set of requirements for lubricating oil indicates that each requirement is likely to be very markedly a function of the chemical constitution of the oil. The manner in which certain physical or chemical properties change with chemical structure can be satisfactorily ascertained only by means of experiments in which substantially pure hydrocarbons of known structure are subjected to appropriate tests.

The accumulation of this desirable information has been greatly handicapped because of the relatively small number and amount of hydrocarbons of high molecular weight which have been synthesized. However, within the past five years, the syntheses of some hydrocarbons of high molecular weight, with values of their properties, were reported by a number of investigators;[1-8] and a notable contribution to this field was made recently by Mikeska,[9] of the Standard Oil Development Company, who synthesized and determined the properties of 52 different hydrocarbons, of high molecular weight, of types which might be expected to be present in lubricating oil. This work of Mikeska's appears to be by far the most extensive and conclusive which has yet been reported, and includes hydrocarbons of 16 to 60 carbon atoms per molecule containing nuclei of benzene, naphthalene, diphenyl, and their hydrogenated products. More work of this kind is extremely desirable.

Among the properties which may be considered in evaluating a lubricating oil with respect to its "service" utility are those of viscosity, change of viscosity with temperature, boiling point, "oiliness," and resistance to oxidation, decomposition, or polymerization.

VISCOSITY

In general, it may be said that, for a given number of carbon atoms in the molecule, the viscosity increases with increase in the complexity of the molecule—whether it be more branching in the side chain, the substitution of shorter side chains for a longer one, or greater cyclization of the nucleus. Unsaturation, through the introduction of a double bond in the side chain, produces a slight decrease in the viscosity; and hydrogenation of unsaturated cyclic nuclei produces a moderate increase in the viscosity.

CHANGE OF VISCOSITY WITH TEMPERATURE

The most generally used measure of the change of viscosity with temperature for an oil is the viscosity index, in which increasing values of the index correspond to decreasing values of the temperature coefficient of viscosity.[10, 11, 16] In general, the viscosity index increases with the length of the side chain in a molecule; and, for a given number of carbon atoms, decreases with increase in the complexity of the molecule—whether it be more branching of the side chain, the substitution of shorter side chains for a longer one, or increased cyclization of the nucleus. The introduction of a double bond into the side chain attached to the cyclic nucleus of the molecule produces a slight increase in the viscosity index. With the hydrogenation of unsaturated cyclic nuclei, the viscosity index remains substantially unchanged.

BOILING POINT

The boiling point of hydrocarbons is primarily dependent on the molecular weight—although, for molecules containing a given number of carbon atoms, there is a significant change with the structure of the molecule. In general, it may be said that the boiling point decreases slightly with the introduction of a double bond in the side chain, and decreases moderately on hydrogenation of unsaturated cyclic nuclei. For a given number of carbon atoms in the molecule, branching in the side chain tends to produce a lowering of the boiling point.

"OILINESS"

The property of "oiliness" of an oil is one concerning which there is much to be learned; and a large number of investigators have been, and are, carrying out studies in this field. It will probably be found that the phenomenon of "oiliness" is the resultant of a number of more fundamental physical properties, each of which will be susceptible of scientific evaluation by more or less simple methods of measurement. The breaking down of the property of "oiliness' 'into its simple components is resulting in a great deal more useful information than the empirical study of the phenomenon as a whole. It will be of interest to learn definitely whether the actual hydrocarbons present in the oil differ from one another in oiliness.

OXIDATION AND DECOMPOSITION

The subject of the resistance of hydrocarbons to chemical reaction by oxidation or decomposition at the temperatures and pressures encountered in an operating engine is a very broad one. While there exists a large amount of data on petroleum oils of various sources and degrees of fractionation, practically no work has been done to determine the susceptibility to oxidation and thermal decomposition of the various types of pure hydrocarbons of high molecular weight. A knowledge of the definite "service" value of the various types of hydrocarbons with respect to stability or resistance to chemical reaction under conditions approximating those of actual service is greatly needed.

The necessity for making such observations under the appropriate "service" conditions is evident when it is realized that the rates of these reactions are markedly

affected by the temperature, and may be greatly influenced by the nature of the metals in contact with the oil.

OTHER PROPERTIES

Other physical properties, which are chiefly important in the problem of identifying hydrocarbons and determining their structure, but which may also be useful in helping to evaluate some of the "service" requirements of oils, include the properties of density, refractive index, melting point, aniline point, surface tension, dielectric constant, and infra-red absorption spectrum. Nearly all of these properties have been, or are, being investigated in various laboratories; and valuable correlations with chemical structure are being made.

Reliable data on the values of these properties may be very useful in two ways: 1, they will aid in the problem of identifying unknown mixtures of hydrocarbons, such as those encountered in lubricating-oil fractions; and, 2, they may provide a measure of the utility of various viscous oils for certain "service" requirements, including those of lubricating, insulating, and other oils.

USE OF PHYSICAL PROPERTIES IN CHARACTERIZING OILS WITH RESPECT TO CHEMICAL CONSTITUTION

Once a complete set of data is obtained on the physical properties of representative compounds of the different types of hydrocarbons of high molecular weight, more certain and effective methods of deducing the type or types of hydrocarbons present in a given lubricating-oil fraction can be established.

In the past six or eight years, for example, a number of combinations involving two or more physical properties has been devised by a number of different investigators; and they have been utilized, in a more or less empirical way (but with surprising success) to characterize petroleum fractions of the lubricating-oil range with respect to their "average" chemical constitution or "predominating" constituents. Such characterizations have been made, in general, only on rather broad lines, because there is too wide a variety of compounds in commercial oils to make a simple and exact relationship possible. Where more effective separation of the material into portions more homogeneous with respect to both size and type of molecules has been made, more exact relationships are possible.

Some of the combinations of physical properties which have been successfully used in the past, and whose effectiveness can be increased in the manner outlined above, include the following: viscosity and density; molecular volume and molecular weight; refractive index and molecular weight; viscosity and temperature; density and boiling point; viscosity and boiling point; molecular volume and surface tension; refractive dispersion and molecular weight; aniline point and molecular weight; aniline point and density.

As our knowledge of the actual constituents of the lubricant fraction of petroleum increases, the usefulness of all such correlations will be materially enhanced.

HYDROCARBON CONSTITUENTS OF THE LUBRICATING FRACTION OF PETROLEUM

As has been pointed out by many writers, no pure hydrocarbon compound has ever been isolated from lubricating oil. The existing knowledge of the hydrocarbon constituents is based solely on a comparison of the properties of more or less closely fractionated cuts of lubricating oil with the values of the properties of pure hydrocarbons of the sizes and types supposed to be in the oil. Until recently the values of the properties of hydrocarbons of high molecular weight were mostly obtained by extrapolation from values for the hydrocarbons of low molecular weight, and this procedure introduced an additional serious uncertainty into the problem of correlating properties.

By the combination of the properties of pure hydrocarbons with the properties of fractions of lubricating oil obtained from a systematic separation resulting in fractions which are no longer easily separable, it is pos-

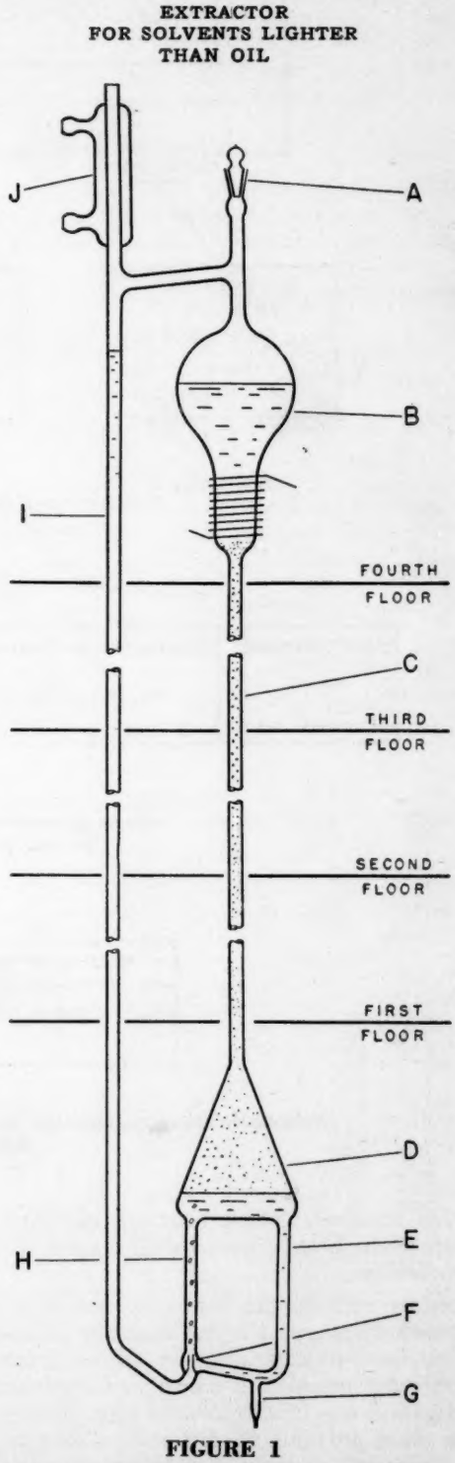

FIGURE 1

Diagram of an All-Glass Extracting Column, 46 feet long, used in the extraction of the "water-white" oil with Acetone (see Mair and Schicktanz[13])

sible to deduce with considerable confidence something concerning the nature of the hydrocarbon constituents of the given fractions. This procedure involves two requirements: 1, having adequate data on the physical properties of the pure hydrocarbons; and, 2, carrying the separation of the lubricant fraction to such a stage that the application of the known processes of separation to the given quantity of material no longer produces any significant change in the physical properties of the given fractions. These fractions can then be said to be substantially homogeneous with respect to size and type of molecules.

A procedure such as the foregoing has been used by the Institute's Research Project 6 at the National Bureau of Standards in separating the lubricant fraction of a Mid-Continent petroleum. The lubricant fraction under investigation was first separated (see Mair et al[12-14]) into three main portions of distinctly different properties: an "extract" portion, by batch extraction with sulfur dioxide; a "wax" portion, by dewaxing at —18° C. from ethylene chloride as solvent; and, finally, a "water-white" portion, by treatment of the remaining oil with silica gel.

The "water-white" oil, which was selected for first investigation, was then subjected to an extended and systematic distillation under high vacuum in order to separate the material into a series of fractions differing with respect to size of molecules. At the conclusion of this extended distillation, each given fraction was expected to contain, for any given type of hydrocarbon, molecules larger than those in the preceding fraction and smaller than those in the following fraction. The stills in which this fractionation was accomplished have already been described.[12]

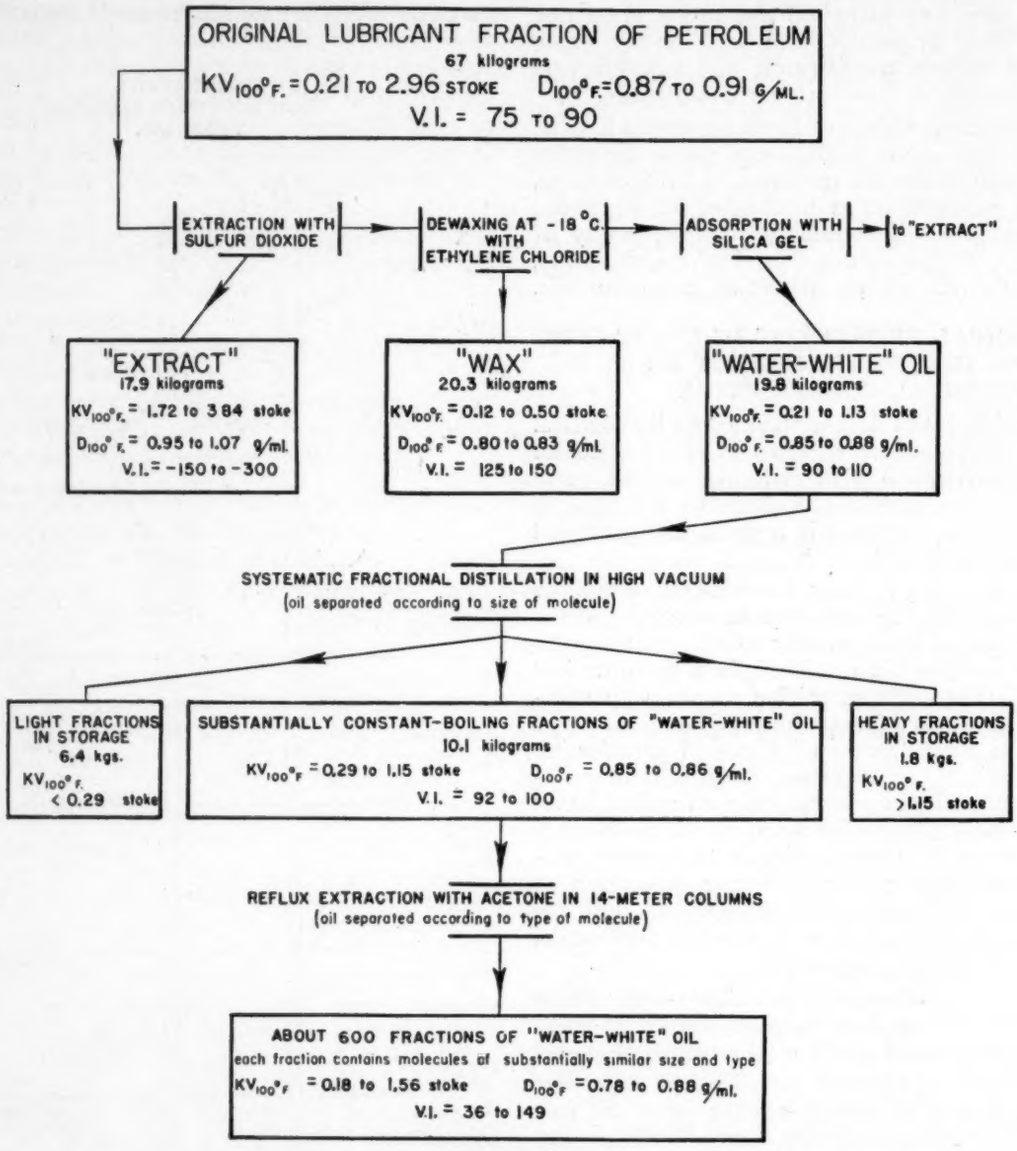
ORIGINAL LUBRICANT FRACTION OF PETROLEUM
67 kilograms
KV100°F. = 0.21 to 2.96 stoke D100°F. = 0.87 to 0.91 g/ml.
V.I. = 75 to 90
EXTRACTION WITH SULFUR DIOXIDE
DEWAXING AT -18 °C. WITH ETHYLENE CHLORIDE
ADSORPTION WITH SILICA GEL
to "EXTRACT"
"EXTRACT"
17.9 kilograms
KV100°F. = 1.72 to 3.84 stoke
D100°F. = 0.95 to 1.07 g/ml.
V.I. = -150 to -300
"WAX"
20.3 kilograms
KV100°F. = 0.12 to 0.50 stoke
D100°F. = 0.80 to 0.83 g/ml.
V.I. = 125 to 150
"WATER-WHITE" OIL
19.8 kilograms
KV100°F. = 0.21 to 1.13 stoke
D100°F. = 0.85 to 0.88 g/ml.
V.I. = 90 to 110
SYSTEMATIC FRACTIONAL DISTILLATION IN HIGH VACUUM
(oil separated according to size of molecule)
LIGHT FRACTIONS IN STORAGE
6.4 kgs.
KV100°F. < 0.29 stoke
SUBSTANTIALLY CONSTANT-BOILING FRACTIONS OF "WATER-WHITE" OIL
10.1 kilograms
KV100°F. = 0.29 to 1.15 stoke D100°F. = 0.85 to 0.86 g/ml.
V.I. = 92 to 100
HEAVY FRACTIONS IN STORAGE
1.8 kgs.
KV100°F. > 1.15 stoke
REFLUX EXTRACTION WITH ACETONE IN 14-METER COLUMNS
(oil separated according to type of molecule)
ABOUT 600 FRACTIONS OF "WATER-WHITE" OIL
each fraction contains molecules of substantially similar size and type
KV100°F. = 0.18 to 1.56 stoke D100°F. = 0.78 to 0.88 g/ml.
V.I. = 36 to 149

FIGURE 2

Schematic Diagram showing the process of separating the lubricant fraction of a Mid-Continent Petroleum

Having been separated according to size of molecules, the fractions were then subjected to a separation with respect to type of molecule, by extended extraction with acetone in tall columns with reflux.[13-15] Figure 1 shows a diagram of one of the 14-meter glass columns used in this extraction.

In Figure 2 is given a schematic diagram of the separation of the lubricant fraction in this manner, and the

TABLE 1

Extraction with Acetone of a Substantially Constant-Boiling Fraction of "Water-White" Oil (Previously Dewaxed and Extracted with Sulfur Dioxide)

Fraction No.	Amt. of Fraction (Percent)	Molecular Weight (Grams per Mole)	Combustion Analysis Moles H_2O / Moles CO_2	In the Formula: C_nH_{2n+x} (n)	(x)	DENSITY AT 100° F. (Grams per Milliliter)	DENSITY AT 210° F. (Grams per Milliliter)	DENSITY AT 25° C. (Grams per Milliliter)	KINEMATIC VISCOSITY AT 100° F. (Stokes)	KINEMATIC VISCOSITY AT 210° F (Stokes)	Kinematic Viscosity Index	Refractive Index n_D^{25}	Boiling Point at 1 MM. (° C.)	Aniline Point (° C.)	Refractive Dispersion $n_F - n_C$ (25° C.)	Specific Optical Rotation (Dextro) D Line (100° F.)
Original charge	100	.....	.....	....	.....	.....	.....	(0.862)	0.3034	0.0494	100	1.4727	....	....	.....	....
1	2.9	(380)	0.8359	27.5	—9.0	.....	.....	.....	0.6259	0.0655	36	1.5032	....	51.6	.....	....
3	3.8	380.6	0.8689	27.6	—7.2	0.8920	0.8508	0.9006	0.5785	0.0656	56	1.4962	204.0	71.6	0.0104	1.85
6	3.9	385.8	0.9490	27.7	—2.8	0.8657	0.8257	0.8741	0.4887	0.0606	64	1.4778	204.0	104.1	0.0087	1.96
14	3.8	385.5	0.9664	27.6	—1.86	0.8516	0.8119	0.8600	0.3281	0.0511	93	1.4717	204.5	107.2	0.0086	1.10
19	6.7	385.2	0.9838	27.5	—0.89	0.8342	0.7941	0.8426	0.2306	0.0438	123	1.4647	205.6	....	.....	0.31
25	3.0	386.6	0.9941	27.6	—0.32	0.8259	0.7857	0.8343	0.2010	0.0414	136	1.4609	208.2	109.7	0.0083	0.11
28	2.7	.....	.....	....	.....	0.8227	0.7819	0.8312	0.1908	0.0404	141	1.4604	....	112.2	0.0084	0.05
29 (last)	5.6	392.4	1.0059	28.0	0.35	0.8193	0.7782	0.8278	0.1808	0.0398	149	1.4587	206.3	113.3	0.0083	....

* These experimental data are from the work of Mair, et. al. tt, 14.

final attainment of about 600 fractions of "water-white" oil of about 15 to 20 grams each. These fractions are probably nearer to pure hydrocarbons than any fractions hitherto obtained from lubricating oil. Two important points are to be noted in connection with the properties of a series of fractions obtained from the subjection of a charge of "water-white" oil (especially of the lower molecular-weight range) to the extraction process: 1, there is little change in the molecular weight of the various fractions obtained — indicating that the extended systematic distillation had done a good job in separating the material according to size of molecules; and, 2, the carbon-hydrogen composition, viscosity, density, and refractive index change markedly from the first to the last of the fractions—indicating that the process of extraction had done a good job in separating the molecules according to type.

In this connection, it must also be remembered that the "water-white" oil, before being subjected to this vacuum distillation and extraction with acetone, was already a highly processed oil, i.e., it constituted but about one third of the crude lubricant fraction, the remainder having been removed as "wax" and "sulfur-dioxide-soluble" material, in nearly equal portions. Each of the final fractions of "water-white" oil was an extremely narrow cut, with respect to both type and size of molecules; and represented about $\frac{1}{4000}$ part of the original lubricant fraction investigated and about $\frac{1}{40{,}000}$ part of the original crude petroleum.

Table 1 gives the properties of the fractions obtained from the extraction with acetone of one of the substantially constant-boiling fractions of the "water-white" oil.

For the fractions of the "water-white" oil of series "A," from the process of extraction with acetone, Figures 3, 4, and 5 show, respectively, the viscosity, viscosity index, and refractive index as a function of the amount of charge extracted.[14] The value of the given

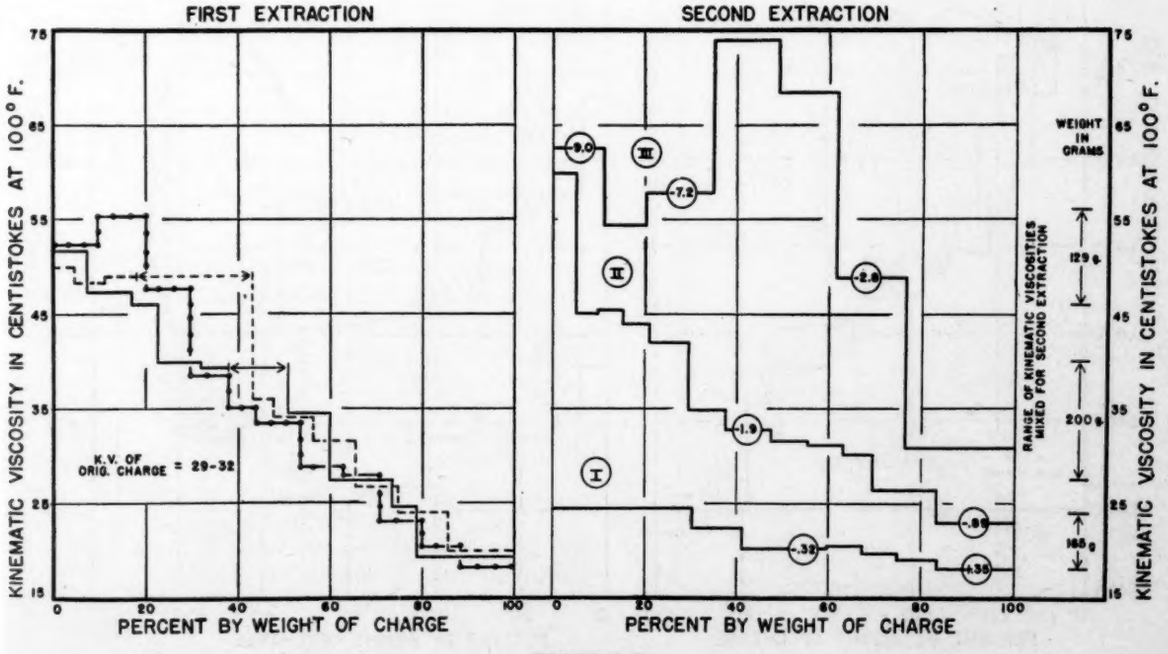

FIGURE 3

Chart showing the viscosity of the various fractions obtained in the extraction of a substantially constant-boiling fraction of "water-white" oil (see Mair and Willingham[14])

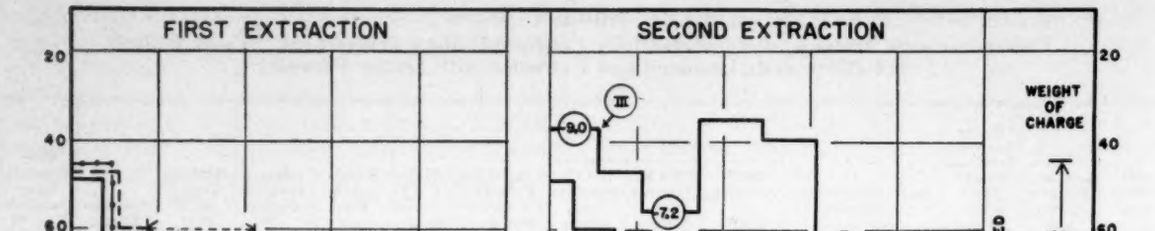

FIGURE 4

Chart showing the viscosity index of the various fractions obtained in the extraction of a substantially constant-boiling fraction of "water-white" oil (see Mair and Willingham[14])

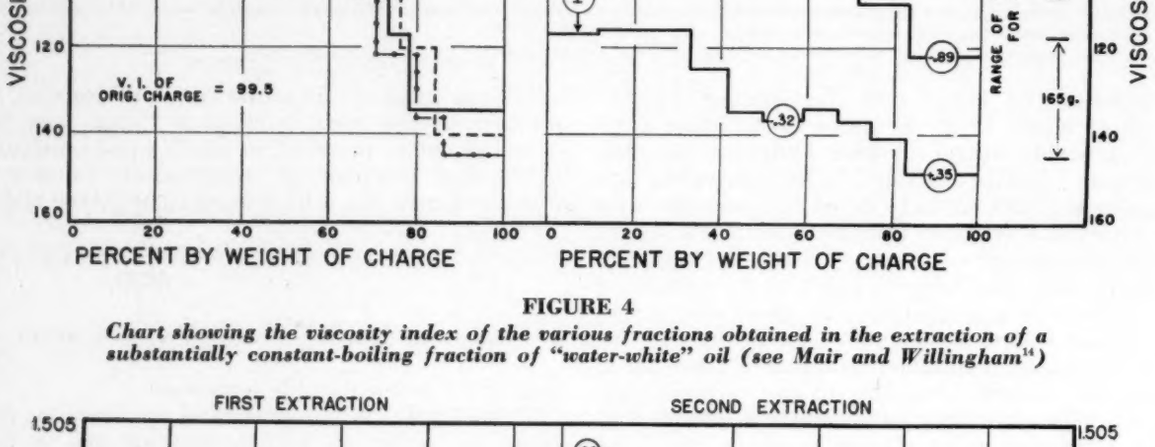

FIGURE 5

Chart showing the refractive index of the various fractions obtained in the extraction of a substantially constant-boiling fraction of "water-white" oil (see Mair and Willingham[14])

property for the original charge of "water-white" oil is also shown.

Of the approximately 600 fractions of the "water-white" oil from the final process of extraction (see figure 3), 30 were selected as "key" fractions, and for these were determined values of the following properties: molecular weight, carbon-hydrogen composition, viscosity at 100° and 210°F., density at 100° and 210°F., refractive index, refractive dispersion, optical activity, aniline point, and boiling point at 1 mm. pressure. The properties of these "homogeneous" petroleum fractions were then compared with those of pure hydrocarbons, of the same molecular weight and carbon-hydrogen composition, with respect to values of viscosity, viscosity index, density, specific refraction, specific refractive dispersion, and aniline point. Figures 6, 7, and 8 show some of the correlations with respect to density, aniline point, and specific refraction.[14]

From these correlations[14] it has been possible to draw the following conclusions concerning the hydrocarbon constituents of the fractions of the "water-white" oil:

1. Of the fractions of lower molecular weight (about 28 carbon atoms per molecule) the least soluble (raffinate) fractions consisted substantially of one-ring naphthene (cycloparaffinic) hydrocarbons, and the more soluble fractions consisted of naphthenes with two (and some with three) rings per molecule.

2. Of the fractions of higher molecular weight (about 37 carbon atoms per molecule) the least soluble fractions consisted substantially of two-ring naphthenes (cycloparaffins), and the more soluble fractions consisted of naphthenes with three (and some with four) rings per molecule.

3. The most soluble fraction in each series appeared to contain some unsaturated hydrocarbons and a considerable amount of one-ring aromatic hydrocarbons.

4. No evidence was found for the presence of *iso* or branched-chain paraffins in the "water-white" oil.

From this information it may be concluded that, when the lubricant fraction of a dewaxed Mid-Continent petroleum is treated by one of the modern solvent-extraction processes, the lubricating oil produced contains no paraffin hydrocarbons, and consists substantially of naphthene (cycloparaffin) hydrocarbons with from one to about five rings per molecule, together with appropriate paraffinic side chains. Highly-processed solvent-extracted lubricating oils from Mid-Continent crude would, therefore, appear to be composed of saturated cyclic hydrocarbon molecules having an appreciable number of the carbon atoms in paraffin side chains.

DO PRESENT REFINING PROCESSES DISCARD SOME DESIRABLE CONSTITUENTS?

One of the important advantages which will be forthcoming from a more definite knowledge of the actual molecules present in the lubricating-oil fractions of petroleum is that of providing a conclusive answer to the question whether present refining processes discard some desirable constituents.

The many different types of solvent-extraction processes which have come into commercial use in the past few years have yielded products greatly improved in many important properties. It is theoretically possible, however, to obtain products which, while better in some properties, might be poorer in others; as it is conceivable that the refining process might not only remove undesirable constituents, but also a particular type of desirable constituent, whose physical and chemical properties are such as to cause it to possess a particularly

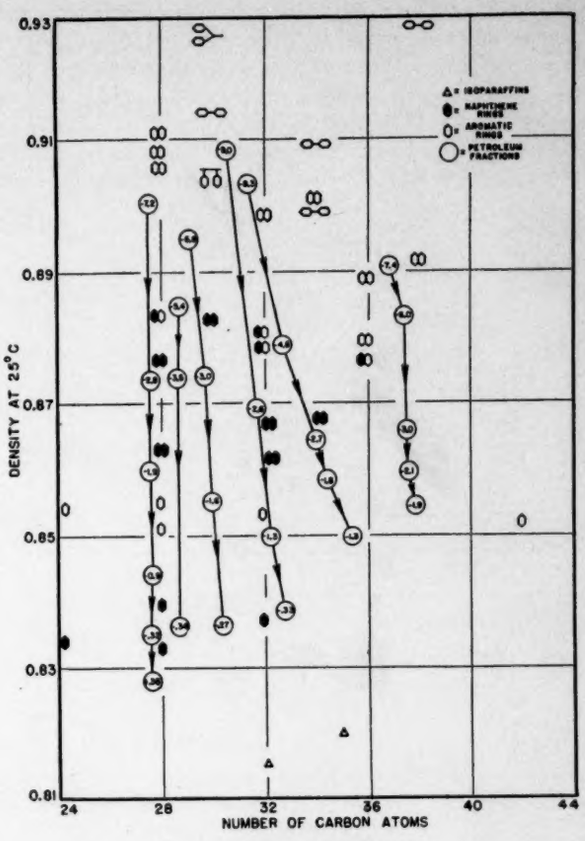

FIGURE 6

Chart showing the densities of the final "key" fractions of the "water-white" oil, together with values for some pure hydrocarbons of high molecular weight (see Mair and Willingham[14])

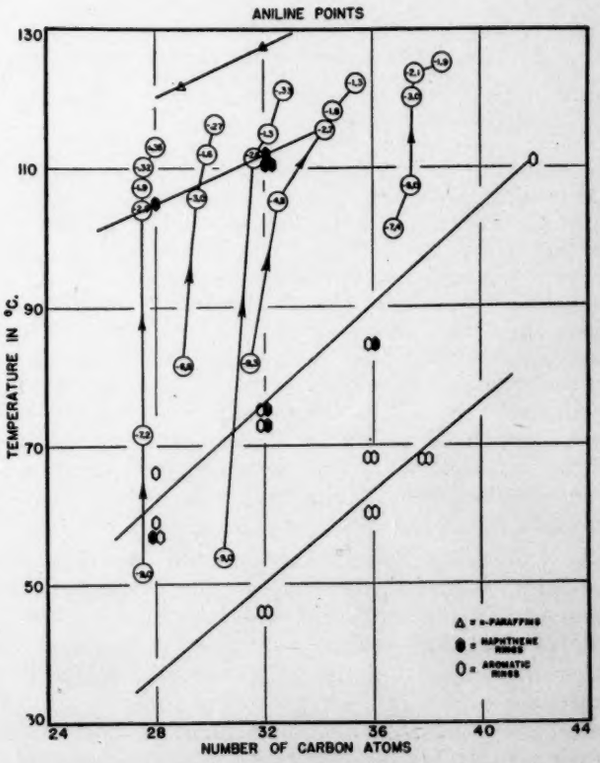

FIGURE 7

Chart showing the aniline points of the final "key" fractions of the "water-white" oil, together with values for some pure hydrocarbons of high molecular weight (see Mair and Willingham[14])

high value in terms of "service" requirements and yet, at the same time, cause it to be segregated, in the refining process, with the undesirable molecules.

An interesting possibility in this connection has been pointed out by Mair and Willingham.[14] It appears that, for aromatic hydrocarbons of one ring and naphthene (cycloparaffin) hydrocarbons of about six or more rings,

CONCLUSION

The work which has been done so far on the lubricant fraction of petroleum by the Institute's Research Project 6 has pointed the way to two important studies. In one of these studies there is being investigated the "extract" or "sulfur-dioxide-soluble" portion (see Figure 3) of the original lubricant fraction, following a pro-

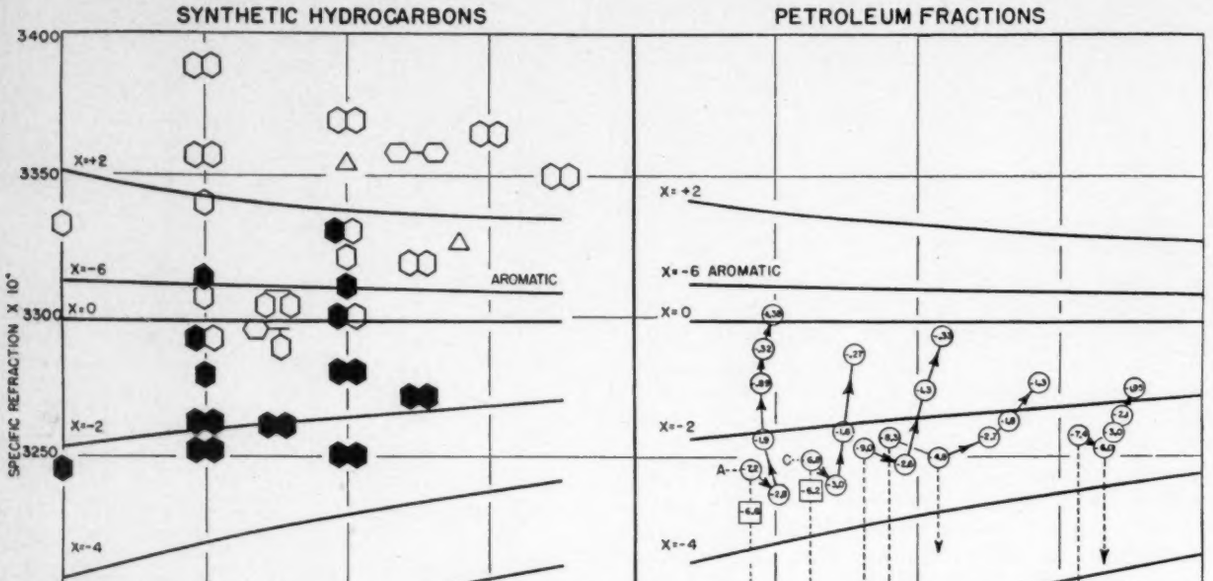

FIGURE 8

Chart showing the specific refraction of the final "key" fractions of the "water-white" oil, together with values for some pure hydrocarbons of high molecular weight (see Mair and Willingham[14])

the solubility relations are so similar as to leave open the possibility of their being segregated together as undesirable constituents, in the extraction processes as carried out at the present time. This would be a questionable situation; since these one-ring aromatic hydrocarbons are known to have high values of the viscosity index, and may also possibly excel in some particular "service" requirements. Such a problem can be resolved by ascertaining definitely whether or not such one-ring aromatic hydrocarbons are actually present in the lubricant fraction of petroleum (the present evidence indicates that they are), and by learning by appropriate tests whether the one-ring aromatic hydrocarbons do possess a high "service" utility for use as lubricating oil.

If it should be found that some desirable constituents are being discarded, then appropriate changes — based upon a study of the physical properties of the given constituents and their relative susceptibility to the various physical processes of separation—may be made in the procedure of the refining process in order to conserve these "good" constituents. Or it might be more feasible to compensate for the eliminated desirable constituents by the addition of appropriate other ingredients.

cedure somewhat analogous to that used on the "water-white" oil. Valuable data are expected from this investigation, especially regarding the aromatic constituents. In another study a closer approach will be made to the separation of pure hydrocarbons from lubricating oil.

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Corrosion Protection In Refineries

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ABSTRACT

THIS paper, based upon a detailed analysis of records, reports, and papers received during the past eight years' activity of the Institute's Committee on Corrosion of Refinery Equipment, discusses the fundamental principles underlying the corrosion of refinery equipment, and summarizes the application of protective measures to such equipment. It is intended to serve as a general guide to those concerned in the protection of refinery equipment against corrosion, and as a record of the protective measures utilized in the past, rather than as a discussion of current or new developments in the field of corrosion protection.

The subject is considered under two general divisions, the first of which relates to so-called high-temperature corrosion and the methods used to protect equipment which is subject to such corrosion. The second part discusses the principles of low-temperature corrosion and protection against such corrosion.

High-temperature corrosion agents and factors affecting high-temperature corrosion are discussed in relation to the chemical properties of metals and neutralizers, and with conclusions based upon theoretical considerations and reported results of tests and usage.

The controlling factors in low-temperature corrosion and protection are explained as an application of the electrolytic theory of corrosion. Summaries of tests and usage of protective methods are given. In concluding each division of the paper, the author, based upon his analysis of the Institute's records, offers recommendations for lines of investigation in the field of corrosion protection of refinery equipment.

THIS paper is the outcome of an invitation of the American Petroleum Institute to examine, analyze, and summarize records, reports and papers received by its Committee on Corrosion of Refinery Equipment since 1928.

During the examination of these data, it seemed that a discussion of the fundametals underlying the two general types of corrosion would be of assistance to those concerned with the application of protective measures in the refinery.

The corrosion reports show that a large number of tests and plant-scale experiments have been made, in addition to careful observations of the rate of corrosion and methods of prevention.

The reasons for the various tests were not always stated; and, therefore, an endeavor has been made in this paper to present in logical sequence the physical, chemical, and metallurgical principles underlying corrosion, so that the cause of any particular example of corrosion and the reason for any particular preventative measure will be readily apparent.

It is first essential, in order that proposed remedies for corrosion be understood, that the broad principles underlying nature's opposition to our unstable requirements be grasped. These fundamental principles are essentially simple in themselves, but confusion arises when we come to apply them to the large variety of conditions met with in the industry. This need not be the case if we keep these principles in mind and apply them logically to each case under consideration.

ARTHUR MARKS, *consulting chemist and metallurgist, New York, read the accompanying discussion at the Division of Refining group session Thursday afternoon, November 12, in connection with the American Petroleum Institute's Seventeenth Annual Meeting at Chicago, Illinois.*

Mr. Marks was graduated in physical chemistry and metallurgy by the Imperial College of Science and Technology, London University, London, England, and pursued postgraduate work in electrochemistry and electrical engineering at Liverpool University. For a period he was in charge of chemical tests at the National Physical Laboratory, and he served on the research staffs of Harland & Wolff, Ltd., and Harper & Bean, Ltd., and as consulting engineer for British manufacturers. Since 1926 he has been engaged in chemical and mechanical engineering in the United States and South America, and currently is making an objective study through analysis of the Institute's corrosion records.

The metals found free in nature are few—the most common examples being gold, copper, and silver. These are characterized by their weak affinity for oxygen and its allied element, sulfur. The chief useful metals are found in nature combined with oxygen and its chemical associates, such as sulfur, viz., iron oxide and sulfide, copper oxide and sulfide, chromium oxide, etc.

The metallurgist extracts or "reduces" the oxides and other compounds to the metal, and presents the engineer with a strong material of construction which is capable of returning to its stable oxidized or sulfurized state at the first opportunity given to it.

Petroleum refining unfortunately supplies favorable conditions to enable the metal to return to its "native" or more stable state.

In the distillation and cracking sections of the refinery, there are volumes of sulfur and sulfur com-

pounds, high pressure, and high temperature, all of which combine to give the best conditions for what may be termed "direct-chemical-action" corrosion.

In the condensing sections of the refinery, the metal is readily attacked by the oxidizing agents, chlorine and water. In this section of the plant consideration must be given not only to the direct action of the chlorine on the pure metal, but also to the influence of impuritjes or different phases of the alloys and metals, which set up electrolytic cells or small batteries in which one portion of the metal dissolves or is oxidized in preference to the other. This type of corrosion is, consequently, designated as "electrolytic corrosion."

In all forms of chemical action, whatever classification may be used, there is some evidence—shown physically, as heat, light, or electricity—of the reaction between the elements and compounds taking part. This may or may not be detected. Thus, for example, if sulfur and iron are heated together, a great quantity of heat is liberated; or, if iron is treated with hydrochloric acid, not only is hydrogen evolved, but also an appreciable quantity of heat is generated.

During the slow electrolytic corrosion of iron in dilute hydrochloric acid, the corrosion is accompanied by the evolution of electrical energy. The electrical potential or force given by the various metals forms a useful guide in the choice of metals in sections of the plant where condensation of water occurs.

In the first case illustrated above, most of the energy of combination of the metal with the destructive element was liberated as heat, the process being rapid; but, if the process is slowed down, electrical energy is liberated, e. g., the electrical energy liberated by the solution of iron in sea water can be detected over a considerable distance through the sea water. An attempt was made during the World War to detect submarines lying still, below the surface, by means of the electrical energy of the corrosion of the hull.

The problem of corrosion in the refinery, therefore, is conveniently considered—both from the nature of the corrosion and the operation of the plant—under two general divisions, as:

High-Temperature Corrosion, or Direct Chemical Action

Low-Temperature Corrosion, or Electrolytic Corrosion.

HIGH-TEMPERATURE CORROSION—DIRECT CHEMICAL ACTION

The parts of the plant affected by high-temperature corrosion are those parts operating above the condensing temperature of water, viz., heating tubes, transfer lines from heater, reaction chambers, flash and rectifying towers.

CORROSIVE AGENTS ENCOUNTERED IN HIGH-TEMPERATURE CORROSION

FREE SULFUR AND SULFUR COMPOUNDS

Free sulfur formed from the decomposition of sulfur compounds in the crude has been shown to have a very great direct action upon iron by E. Retailliau and F. R. Lang[1] in a carefully conducted series of experiments. There is no doubt of the direct action of sulfur on iron in the absence of moisture. On the other hand, there is evidence that a water film may play a part in some high-temperature and high-pressure operations. Where for example, calcium hydroxide ($Ca(OH)_2$) or sodium hydroxide (NaOH) is introduced into the system as a neutralizer, the water thus added may play an important part which will be discussed under the heading of neutralizers.

An analysis of the series of tests of some 25 ordinary and special steels conducted in various plants by the committee does not show any direct relation between the amount of corrosion and the percentage of sulfur in the crude; in fact, certain crudes relatively low in sulfur showed greater attack on the steels than some crudes higher in sulfur.

A most interesting series of tests on this point was conducted by placing blanks of SAE 1020 steel in a Cross reaction chamber and in a Dubbs reaction chamber—the former running a crude containing 0.685 percent sulfur, and the latter running a crude containing more than 1 percent of sulfur. The only other variable factor in these tests was the pressure, which is discussed later.

The mean loss of metal for all the samples in the former case was 17.5 g. per 1,000 hours' exposure, and in the latter case 7.98 g. per 1,000 hours' exposure. This is a convincing illustration of the fact that the percentage of sulfur in the crude is not necessarily a direct measure of its corroding power—a conclusion with which every experienced chemist will agree.

This would indicate the probability of the sulfur playing a cyclic function in the attack on the iron, and further laboratory and plant researches along the lines of the work of Messrs. Retailliau and Lang would help in the complete elucidation of the part which sulfur plays in the destruction of the metal. In the meantime it can be stated that, whether direct or indirect action occurs, it is probably the most active material encountered in high temperature corrosion.

The work of Wood, Sheely, and Trusty[2] with solutions of various sulfur compounds in naphtha at room temperature is also of importance. They showed that:

a. Mercaptan sulfur is most corrosive, forming mercaptides of iron and copper.
b. Hydrogen sulfide is very reactive, forming iron and copper sulfide.
c. Free sulfur is quite inactive with iron, but corrodes copper and brass.
d. Other sulfur compounds are only slightly corrosive.
e. In all cases corrosion is accelerated by the presence of water.

Other investigators, as for example Wilson and Bahlke,[3] have shown that free sulfur and hydrogen sulfide are very active above 700 deg. F., but their action is negligible below 500 deg. F. The coating of iron sulfide formed slows down the reaction, but does not stop it completely. The scale is loosened by heating and cooling, and by erosion.

Although the sulfur content of the oil cannot be accepted as an indication of the corrosion rate, as shown above, the general conclusion is that high-temperature corrosion is caused by free sulfur, mercaptans and hydrogen sulfide, which are products produced by the high temperature of the stills on the more complex sulfur compounds originally present in the cold feed. Further work is desirable at high temperature and pressure to investigate the part which steam may play in the reaction.

NAPHTHENIC ACIDS

Recent work has shown that organic acids may be an important factor in high-temperature corrosion of equipment handling California crudes.

Seligman and Williams[4] have shown that organic acids—such as acetic, proprionic, palmitic, stearic, and

oleic—react with aluminum at a low corrosion rate at 200° F., but at 570 F. the reaction is quite rapid.

The reaction rate is apparently independent of oxygen concentration, but is greatly influenced by the presence of water. The addition of 0.05 percent of water practically stopped corrosion, due, no doubt, to the formation of a stable oxide film which is relatively insoluble in acid and alkalies. These results must be interpreted in the light of the relative solubility of aluminum oxide in acid and alkali, as hot acid and hot alkali will dissolve aluminum oxide. This question of relative solubility and mass of the reacting materials is too frequently lost sight of. For example, barium sulfate is relatively insoluble in water—in fact, one of the most insoluble substances—and in dilute ferric chloride; but its solubility in more concentrated solutions has led to some great blunders in the determination of sulfur in steels. Although the work of these researches deals with aluminum, the reactions are also possible with iron; and a knowledge of the work of the food-packing industry on this subject would, no doubt, be helpful—the carboxylic group (COOH) containing a replaceable hydrogen atom, would at once be suspect in high-temperature corrosion.

Vuiborov[5] has shown that naphthenic-acid corrosion is experienced with Russian crudes, and Blount[6] has shown that the asphaltic crudes of California containing naphthenic acids are very corrosive at high temperature—the lower-molecular-weight acids being more active than the higher-molecular weight acid, from light and heavy lubricating distillates, respectively.

Laboratory tests showed that the pure acids at 650 deg. F. penetrated steel specimens 0.058 inch per year at 5.5 percent concentration, and 0.203 inch per year at 16.5 percent concentration. Copper alloys were more resistant than steel, and the chrome steels were practically inert to naphthenic-acid corrosion.

The influence of corrosion products in the refined product is also important. Blount[6] has shown that copper naphthenate and copper mercaptide, with pressure distillates containing as low a concentration as one part per million, produce striking degradation in color. Several corrosion reports show that less doctor reagent is required in treatment after neutralizers have been used in processing.

INORGANIC ACIDS

The principal inorganic acids met with in processing are hydrochloric and sulfurous acids, which are active in the presence of water. Hence, their effect is mainly noticeable in the lower-temperature sections of the plant, such as in the rectifying towers. Any action they may have in the high-temperature sections of the plant is, no doubt, masked by the more active elements in those sections.

FACTORS AFFECTING HIGH-TEMPERATURE CORROSION—PHYSICAL OR MECHANICAL

The factors influencing high-temperature corrosion are probably as complex as the nature of the chemical reactions taking part.

PRESSURE AND TEMPERATURE

An examination of the steel corrosion tests conducted by the committee in various plants failed to show any direct relation, except perhaps in the case of plain carbon steels, SAE 1020, used as comparison blanks.

The mean temperatures in the two series were approximately 900 deg. F., with a variation of 20 deg. to 25 deg. above and below this figure. The pressures were, however, 700 lb. where the rate of corrosion was 17.5 g. per 1,000 hours' exposure to crude containing 0.685 percent sulfur, and 175 lb. where the rate of corrosion was 7.98 g. per 1,000 hours' exposure to crude containing more than 1 percent of sulfur.

These results would indicate that pressure is the primary factor in the corrosion. Probably the hydrogen-sulfide gas is the active agent being compressed or generated under pressure. One has only to correlate these figures with the modern pressure processes for the synthesis of ammonia to realize that both pressure and temperature may play a more important part in the corrosive process than the actual percentage of reacting substances, such as sulfur; as there is always present more sulfur even in the low-percentage crudes than it is desired to see taking part in the corrosive action, as evidenced by the flow of the excess to subsequent parts of the plant.

The results stated above showed that increasing the pressure by four times doubled the corrosion, even in the presence of a smaller quantity of sulfur.

TURBULENCE

This is a secondary effect, in that it removes the products of corrosion from the surface of the affected part by mechanical action. So far as known, there is no case of erosion where, in the final analysis, the mechanical effect was the primary cause of the loss of metal—excepting, of course, cases where abrasive substances are deliberately introduced into the stream, such as in sand blasting. The increased velocity and change of direction of the fluid washes off the corrosion products, and to some extent the corrosion products may themselves be soluble in the oil flowing through the tubes. Cleaning tools also remove the protective film, although in some cases it is noted in the corrosion reports that the tools used are of such a nature that they are, in the opinion of the operators, not responsible for their excessive corrosion figures.

The turbulence depends upon the skin friction of the pipe, the speed of flow above that normal for the particular liquid and "pipe-skin" effect, the changes of contour of the pipe, the presence of unfilled gaps at joints, the partly vaporized condition of the stream, and like factors. To reduce turbulence to a minimum is a question of correct design and execution in relation to speed of flow and pressure drop. It is obvious that the commercial as well as the physical factors are considered by the designer, and the metallurgist has given him adequate help in the solution of his problem as indicated by the corrosion reports.

EROSION

Several reports from members deal with erosion of headers in tube furnaces. This case may be profitably considered in detail.

When the oil flows through the straight portions of the tube in a tube still, the particles of oil close to the wall of the tube are slowed in their travel by the skin friction of the surface of the tube, which is greater than the friction between the particles of the oil. Hence, there is a natural tendency for the remainder of the oil being prevented from making contact with the surface of the tube. The number of particles touching the surface of the tube at any section will, therefore, be proportional to the internal circumference of the tube.

When the oil reaches the header, a change of direction occurs, and the straight streamline flow is upset. Particles at the center and between the center and circumferential row of particles flow to the circumference, so that the sum of all the particles of oil at the cross-section can now make contact with the metal. Since

in any chemical or corrosive action the amount of action is proportional to the reacting masses, a much greater contacting of oil per square inch of metal surface occurs at the header than in the tube and, hence, a much greater corrosion.

In this connection, consider as a contrast a case of pure erosion, as for example, in a sand-blasting plant. Here the particles of sand move in a stream of air with no cushioning or lubricating effect. The particles of sand themselves are inelastic (for practical purposes) and, hence, the force developed by their sudden stoppage by a surface of metal may rise to infinity. As is well known, the action is sufficiently powerful to erode or to break off mechanically particles of steel from a steel surface.

This may occur in still tubes owing to the loosening of fine coke particles on re-cycle of cracking stock. Its action is modified according to the degree of vaporization occurring. In a complete liquid-phase process the oil will tend to cushion and lubricate the particles striking the wall of the header, but there is obviously the probability of mechanical erosion by the coke particles. The substitution of a cast chromium-steel header gives increased resistance to both erosion of this kind, on account of its greater hardness, and also to corrosion on account of its more inert chemical character.

GENERAL CONCLUSIONS RELATING TO HIGH-TEMPERATURE CORROSION

The general conclusions regarding high-temperature corrosion may be summarized briefly:

1. Sulfur and its compounds are the primary reactive substances.
2. Their influence is a function of temperature and pressure, rather than of percentage of sulfur in the material being processed.
3. The higher pressures, coupled with the high temperature in liquid-phase cracking, result in local overstress of the metal and increased rates of corrosion.
4. Mechanical erosion, due to loosened coke particles travelling at high velocities, may increase the rate of corrosion where a change in direction of flow occurs owing to actual mechanical removal of protective corrosion products.
5. The influence of moisture in the crude should be studied further. In this connection, the remarkable economic results in blast-furnace practice for the manufacture of pig iron, by removal of water from the air entering the furnace, are deserving of close consideration.

PROTECTIVE METHODS FOR COMBATING HIGH-TEMPERATURE CORROSION

USE OF CORRECT MATERIALS OF CONSTRUCTION

As has been indicated in an informal manner during the discussion of corrosion, a primary factor of corrosion is the tendency of the metals to return to a more stable state under the conditions in which they are giving useful service.

The natural course would, therefore, be to seek for a material which is stable or is highly resistant to attack by corrosive agents. Considerable advance has been made in this direction, owing chiefly to the demands of the synthetic-ammonia and the oil-cracking industries.

The ancient injunction, "seek and ye shall find," is still true, and the findings are infinitely greater owing to the simultaneous development of research tools, so that results of the searchings are accruing at a compound-interest-law rate.

The chemical factor which has to be met in high-temperature high-pressure processes in the refining industry is the affinity of sulfur and its compounds for the metals.

In the high-temperature sectons of the plant, therefore, metals are required of adequate mechanical strength so that the metal thickness will not be unduly great, and consequently, have a high temperature-stress factor, and be heavy and expensive. The structural form must comply not only with adequate capacity, but with a minimum bending and creeping at the high temperatures used, and a maximum bursting resistance to withstand the pressures.

Once the high-temperature strength factors are known, these structural requirements can be calculated.

The heat of formations of the sulfur compounds of the metals may be taken as a guide in their choice; but in the first place, naturally the engineer has taken the cheapest and strongest metal for construction, viz., steel, and asks for improvements as temperatures and pressures are increased.

Considering a few of the common metals in regard to the heat of formation of their sulfides, these have been determined experimentally or calculated from experimental data, as in Table 1.

TABLE 1

Metal		Heat of Formation of Sulfide (Calories)
Aluminum	$Al–Al_2S_3$	+126,400
Iron	$Fe–FeS_2$	+ 35,600
Iron	Fe–FeS	+ 23,060
Lead	Pb–PbS	+ 22,200
Copper	$Cu–Cu_2S$	+ 18,970
Nickel	Ni–NiS	+ 17,390
Copper	Cu–CuS	+ 11,610

The metals which unite with sulfur, forming sulfides with low heat of formation, readily form sulfides; and, conversely, the sulfide readily undergoes decomposition.

For instance, in the case of the most useful commercial metal iron, the sulfide easily forms under increasing temperature and pressure, but is also easily decomposed at the same temperature by reducing the pressure below that of the atmosphere.

Aluminum with a high heat of formation of its sulfide has been tried as a lining for expansion chambers and drums subject to corrosion by sulfur gas, but not with any marked degree of success as reported in the corrosion reports—due, no doubt, to other factors, particularly the mode of applicaton, etc.

The most successful material so far tried has been the high-chromium iron alloys. These are both resistant to sulfur corrosion and, by the addition of suitable quantities of nickel and reduction of the carbon content to a minimum, are, generally speaking, structurally strong.

Chromium-nickel-iron alloys have therefore, been used with considerable success as still tubes and as linings for the vapor space of forged-steel drums and reaction chambers, but have not been universally favored.

The loss of metals may be due not only to direct combination with sulfur, but also to the part which oxidizing agents, such as water, may play in the high-temperature parts of the plant.

The heat of formation of the oxides of the metals may, therefore, be considered in this connection.

The results of the corrosion committee's experiments

may be usefully considered in the light of these figures.

For example, simple nickel-iron alloys, and high-nickel with low-chromium content alloys, were among the group of highly-corroded metals—which result would be anticipated from Table 2.

The figures for the heat of formation of the oxide of chromium, together with its high-tensile properties, are confirmed by both the corrosion committee's tests and by experience. With regard to aluminum, the results have been successful in some cases and failures in others. For example, "calorized" tubes of recent manufacture appear in some reports as giving satisfaction. In this connection, the low density of aluminum should not be overlooked.

The border-line results shown by the molybdenum and tungsten steels indicate the need for further development by the addition of increasing percentages. Apart from their direct influence, their indirect influence in dissolving carbon, and so preventing the deposition of carbides on the crystal boundaries of the alloy during continued heating is important.

TABLE 2

Metal		Heat of Formation of Oxide (Calories Per Gram)
Aluminum	$Al-Al_2O_3$	389,490
Chromium	$Cr-Cr_2O_3$	267,390
Titanium	$Ti-TiO_2$	217,400
Silicon	$Si-SiO_2$	201,340
Tin	$Sn-SnO_2$	138,100
Molybdenum	$Mo-MoO_2$	131,400
Tungsten	$W-WO_2$	126,200
Manganese	Mn–MnO	90,800
Iron	Fe–FeO	64,040
Nickel	Ni–NiO	57,830
Lead	Pb–PbO	52,473
Copper	Cu–CuO	34,890

The usefulness of tin is indicated, but its low melting point and mechanical characteristics probably preclude its use in high-temperature service.

In combination with copper and zinc, tin has performed great service, and its value will be seen under the discussion of low-temperature protective methods.

The heat of formation of the oxide of titanium, together with its high melting point of 1,800 deg C., indicates that useful investigations — in addition to what has already been done—are desirable.

Frequent references are made in the corrosion reports to the presence of magnesium chloride in the crude from which hydrochloric acid is formed by dissociation. The heat of formation of the chlorides of the metals in connection with their resistance to corrosion in high-temperature parts of the plant should be considered. Water is frequently present (Table 3).

One of the most important questions in high-temperature corrosion relates to whether conditions in the heater tubes, reaction towers, and drums is oxidizing or reducing. The presumption generally is that the conditions are of oxidizing character.

The major reaction taking place is that of the direct union of sulfur with the metal. On the other hand, views have been expressed as to the possible action of aqueous films, and these are entitled to consideration. The presence of water or steam at the high temperatures used would indicate the possibility of the formation of sulfuric acid by oxidation of the sulfur which attacks the iron to form a sulfate which is subsequently decomposed. Sulfate of iron is readily decomposed at relatively low temperatures, and the fact that the final product is iron sulfide does not preclude the possibility of this cycle reaction. In this connection, the varying results reported with calorized tubes are worthy of further investigation.

The corrosion reports show different degrees of success and failure with alloy steels, and there is no general and decisive view as to the economic necessity for any particular composition.

Some reports show that technical and economic requirements are met with 18 Cr-8 Ni steel, while others

TABLE 3

Metal		Heat of Formation of Chloride (Calories Per Gram)
Chromium	$-(CrCl_3 \cdot 4H_2O)Cl_2 \cdot 6H_2O$	845,010
Chromium	$-CrCl_3$	139,550
Chromium	$-CrCl_2$	99,640
Aluminum	$-AlCl_3 \cdot 6H_2O$	641,820
Aluminum	$-AlCl_3$	166,800
Silicon	$-SiCl_4$	149,100
Copper	$-CuCl$	195,030
Copper	$-CuCl_2$	51,422
Manganese	$-MnCl_2$	112,690
Iron	$-FeCl_2$	81,864
Iron	$-FeCl_3$	96,300
Tin	$-SnCl_2$	81,147
Tin	$-SnCl_2 2H_2O$	233,700
Tin	$-SnCl_4$	127,400
Titanium	$-TiCl_4$	183,500

show preferences for both 4-6 Cr and plain carbon steel. Carbon-molybdenum tubes are preferred for high temperatures with little corrosion, and chrome-molybdenum tubes for corrosive conditions in cracking stills.

It is evident from the corrosion reports that the steel which most economically meets the corrosive action of the particular crudes being handled is the one to use. Generally speaking, there is no majority tendency toward the use of high chromium-nickel alloys. Some members have not found calorized tubes better than plain carbon steel, while others show satisfactory results by the use of 4-6 percent chromium steel, with 0.4 to 0.6 percent of molybdenum. Other chromium steels are on trial.

It would probably be an advantage to have a definite maximum depreciation figure per 1000 barrels of distillate gotten out as a guide in the choice of the more expensive metal with its increased life.

In the large-diameter sections of the high-temperature plant, such as expansion and reaction chambers and drums, both linings of high-chromium steel and plain carbon steel with chromium plating have been tried. The greatest practical difficulty encountered has been in the correct attachment of special linings. Coke is formed between the lining and the walls of the chamber, with resulting buckling and inefficient contact; but, nevertheless, quite advantageous results have been obtained.

One report — on the use of 18 Cr-8 Ni plates in forged-steel tube drums giving a life of 18 months—favors the use of corrosion-resistant metal of this composition. Other reports indicate that successful protection can be obtained with sprayed aluminum, where the aluminum is put on with the electric torch and not with the oxyacetylene spray.

Anyone familiar with the oxidizing action of the spray gun will at once see that the metal was probably oxidized and ruined before it was put to use; the electric torch, being much less oxidizing than the oxyacetylene torch, gave a successfully coated surface.

Chromium plating has been tried with some success

in large high-temperature vessels. Considerable improvement has been effected in the application of chromium plating by improvments in the electrolyte and the distribution of the anodes when plating. The greatest defects in chromium plating have been the formation of pin holes and lack of adequate contact with the steel. The majority of the corrosion reports indicate that the most practical and successful method of protection has been by the use of metal linings attached by riveting and electric welding.

Non-metallic linings have been used in some high-temperature sections of the plant, soaking drums having been lined with 2 inches of concrete with successful results. Fractionating towers have been successfully lined with both gannister and acid fire brick, as well as with cement attached to the tower by means of expanded metal. An "acid-character" material such as gannister would be theoretically the better type, as the neutralization of alkali in a cement lining results in "spalling"—which anticipated result is indicated as having occurred in several reports. The action of magnesium salts on concrete would also anticipate the probability of spalling occurring, in view of the reported presence of magnesium salts in many crudes.

ADDED CHEMICAL REAGENTS—NEUTRALIZERS

The use of a neutralizer is probably the simplest and most practical method of suppressing corrosion. This is shown clearly in the corrosion reports.

The three neutralizers employed in various plants were caustic soda, lime, and soda ash.

The chemistry of the process of neutralization as applied to high-temperature corrosion probably includes the following reactions:

1. Combination of the neutralizer with sulfur and sulfur compounds.
2. Suppression of the hydrolysis and dissociation of the less stable chlorides.
3. Neutralization of the naphthenic acids.

Caustic soda and caustic lime unite with sulfur and with hydrogen sulfide. The reactions occurring may be expressed by the equations:

$$NaOH+S=Na_2S+H_2O$$
$$Na_2S+S=Na_2S_2, \text{ etc.}$$
$$NaOH+H_2S=NaHS+H_2O$$
$$NaOH+NaHS=Na_2S+H_2O$$

The majority of the reports show a preference for using lime rather than caustic soda or soda ash. It is the cheapest, but sometimes results in off-specification fuel oil. A consideration of the heat of formation of the sulfides may be of value in connection with these results.

HEAT OF FORMATION OF THE SULFIDES

Metal Sulfide	Heat of Formation (Calories Per Gram)
Sodium sulfide—Na_2S	44,100
Calcium sulfide—CaS	114,820
Ammonium sulfide—$(NH_4)_2S$	6,200
Ammonium hydrogen sulfide—$(NH_4)HS$	42,400

It will be seen that the sodium sulfide is more readily formed, but not so stable as calcium sulfide; and that calcium oxide (lime) is theoretically the best neutralizer to use. The general conclusion from experience is that caustic soda is more efficient than calcium oxide (lime), combining more readily with sulfur and also improving the quality of distillates; but precautions against embrittlement of the steel, degeneration of fuel-oil and asphalt quality are necessary. Ammonia is not satisfactory in high-temperature portions of the plant—the sulfide being less stable and, if formed, readily dissociated. The use of caustic soda undoubtedly introduces serious operating hazards and, hence, the general practice has tended toward the use of lime as the most practical neutralizer for high-temperature corrosion. The report of the Sub-Committee on Neutralizers, of November 9-11, 1931, deals fully with the subject.

The problem of caustic embrittlement of the steel has been investigated by Williams and Homerberg,[7] and others. Generally, the tendency has been to attribute the action to the absorption of hydrogen and the reduction of sulfides and oxides at the crystal boundaries of the metal. While this action may be true, the simple explanation that there is alkali corrosion occurring during which the segregates and impurities at the boundaries are dissolved is the more probable explanation—an alkali-corrosion cell being formed. The suppression of caustic embrittlement, by suitable treatment of the metal in the course of manufacture has been held back by the ancient specifications for the numerous varieties of boiler plate on the market under the various names of "still" steel and the like. The idea that a dead soft steel is the best for resisting alternating stress is still prevalent in the mind of the mechanical engineer who overlooks the fact that not only caustic embrittlement, but also alternating-stress fractures, start at places of minor weakness in the steel, i. e., at slag lines and at crystal boundaries where impurities thrown out during crystallization are deposited.

QUANTITY OF NEUTRALIZER REQUIRED

Lime: The reports show that most of the refiners used between 0.1 and 1.5 pounds of lime per barrel of crude charged, and in one case (Kansas crude) as low as 0.02-0.03 pound of lime per barrel of crude.

The amount added has been controlled generally by the condition of the coke, working for coke deposits which are just alkaline. The net result in the corrosion loss has been stated to be a reduction of from 25 percent to "complete inhibition of high-temperature corrosion"—the latter statement being made in regard to the cracking of high-sulfur oil. One operator who used from 0.6 to 1.5 percent of lime reported that the quantity used was too much. In that case, protection of heater tubes and towers was from 80 to 95 percent effective.

Caustic soda: This is introduced in water solution of from 15 degrees to 25 degrees Baume gravity. The quantity used varies from 0.09 to 0.25 pound per barrel processed.

Chamber corrosion was reported as being reduced 48 percent, and in other cases iron in the distillates was reduced 80 percent. One case reported corrosion entirely eliminated, and another case reported one severe failure due to caustic embrittlement.

The quantity required is less than in the case of lime, and appreciable improvements are reported in the distillates. The "spent" caustic soda left in residual oils gives trouble in slagging of furnace walls, where residues are burned as fuel.

It would be of advantage in the discussion of this problem if figures were available showing the condition of the residue in the coke, i. e., to what extent the alkali is in the form of sulfide, oxide, sulfate, or salts of naphthenic acids.

No doubt some members have investigated this question, and the information if available would be of value.

Ammonia: The low heat of formation of ammonium sulfide would at once indicate the probable ineffective

value of this alkali in high-temperature corrosion protection. Where adequate quantities of water are present for the direct formation of ammonium hydrosulfide, its use would be indicated. In practice it has shown itself inadequate and practically ineffective, but its use gave protection in the low-temperature portions of the plant by passing over with the distillates.

PROTECTION BY MEANS OF "FILMS"

The application of films for the purpose of protection from corrosion is a familiar matter in regard to atmospheric corrosion, which is discussed later under the question of low-temperature corrosion. The problem of protective films under high-temperature conditions needs to be examined from another angle.

The most illuminating example of protection by films in the refinery is found where films of coke are formed, such as in still tubes and high-temperature drums. These films prevent contact of the oil with the metal, but suffer from the defects of other film-protection methods. The films of coke are highly non-conducting and, hence, tend to cause overheating of the tubes; they are porous and, hence, permit the slow diffusion of oil to attack the metal. They increase rapidly in thickness, due to the increasing temperature, etc., until finally their thickness becomes such that a shut-down is necessary for their removal.

In addition to these decomposition films there are corrosion films to consider. The remarkable resistance to corrosion of the chromium alloys has been attributed to the formation of protective corrosion films. This view is probably erroneous. As discussed above, the working temperature is below that at which chromium is attacked readily by sulfur. Some metals, such as iron, as shown by various researches, are attacked at comparatively low temperatures; and others, such as copper and silver, at atmospheric temperatures.

In the case of aluminum which forms an oxide readily in the air, the oxide being relatively insoluble in water, a protective surface is formed on the aluminum. Similarly, there is the well known "passive" state in which a metal, like iron, for example, in a strong acid is protected by the formation of an oxide film or high oxygen-metal-concentration film. While this is true in these cases, the application of this theory to other cases where other factors of greater importance are present has been overdone. The extent to which this has been carried may be realized by the fact that it has been considered necessary to reduce the thickness of the protective film to a few molecules of thickness, owing to lack of evidence of its presence; whereas the straightforward explanation that the conditions present do not warrant any action is often ignored. Insofar as protective films formed by oxidation of the metal are concerned, they may be dismissed when considering the lesser corrosive action occurring when a chromium alloy is substituted for a plain carbon or a nickel steel. The explanation of the superior resistance of chromium to sulfur and acid corrosion is probably due to its more inert character at the temperatures now used than to its forming protective films on its surface.

Whatever explanation is found ultimately to be the correct one, the influence of the protection afforded by increasing chromium content is undoubted.

RECOMMENDATIONS FOR LINES OF INVESTIGATION

Progress is essentially the result of an attitude of mind combined with an adequate grasp of the fundamental facts. For example, in considering high-temperature corrosion, it has been shown that the metals may be arranged in order of the heat of formation of their oxides, and consideration of these figures would indicate the uselessness of investigating nickel alloys as high-temperature corrosion-resisting metals. On the other hand, the influence of nickel on the mechanical properties is a well established fact; and, hence, it may be necessary to incorporate this element in an alloy for the mechanical effect of increasing the elasticity of a hard material.

The recommendations for lines of investigation in connection with the suppression of high-temperature corrosion may be considered under the following sections:

Distilling Process
Structure of Plant
Composition of Metal or Other Materials of Construction.

DISTILLING PROCESS

The fundamental requirements for a distilling process are heat and reduced pressure. The function of the application of heat is to raise the vapor pressure of the liquid to that of the atmosphere; at this vapor pressure the liquid boils. This can be assisted by reducing the pressure of the atmosphere in the distilling vessel or by the application of Dalton's law. In recent years the principle of reducing the pressure of the atmosphere has been applied to bubble towers, some of which work under high vacuum.

The majority of the stills in modern practice demand a high pressure to give a rapid flow through the tubes, of the order of 13 feet per second, and also for other reasons—hence, the higher rate of corrosion from sulfur and sulfur compounds, whose activity appears to bear a definite relation to pressure. As far as the process is concerned in relation to corrosion, the following investigations are suggested:

The solubility of sulfur and sulfur compounds in various crudes.

The fundamental nature of the sulfur compounds in the various crudes and their physical and chemical characteristics. Some work has already been done on the first and second investigations.

Variation of solubility of sulfur and sulfur compounds in the crude with temperature and pressure.

Based upon the first and third, investigation of the problem of bleeding the sulfur after the pre-heater.

Investigation of the nature of the reaction with neutralizers in presence and absence of water. An examination of the condition of the sulfur in the coke would, no doubt, assist in elucidating the function which water is performing in the corrosion, if any.

Assuming for the moment that water plays a part in the high-temperature corrosion, investigation of methods of removal of water seems desirable.

STRUCTURE OF PLANT

The development of the tube still in modern times has shown a grasp of the fundamentals of heating a liquid by increasing the surface exposed to radiant heat in relation to the volume. Apart from its influence on the product of distillation, pressure has been applied to give a volume efficiency, etc., to the plant resulting in increased corrosion. Possible modifications of plant structure insofar as it may affect corrosion should be considered.

Tube headers are shown by the corrosion reports to have excessive corrosion due to turbulence at these points. A study of the influence of the form

of header is indicated, and tests would be usefully made on the comparative influence of circular headers and parabolic headers. These two types of headers could be constructed in glass by people who have experience in heavy-glass-tube manufacture for industrial use. Actual visual observation of the character of the phenomena of turbulence could be studied in this manner.

The influence of coke upon the rise in temperature in the metal of the tubes is well known. The allowable thickness of coke deposit for the various steels is also known, varying from about 0.05 inch for a carbon steel to as high as 0.4 inch for some of the special steels—this allowable thickness of coke depending upon the creep strength of the steel. It might, therefore, be of value to know the relation between tube diameters and coke formation for the various crudes at various speeds of flow, and also the temperature and pressure relations for coke formation with various crudes.

The nature of the passage of the corrosive sulfur and sulfur compounds through the oil film, and subsequent coke deposit in still tubes, would also appear to be of value to the refiner. Is the process of sulfur corrosion taking place through the protective coke skin one of diffusion or chemical decomposition? Thus a knowledge of this question might assist in the solution of the corrosion problem by introducing a protective skin of different character, but of high heat conductivity such as is brought about when using lime as a neutralizer—the alkali in the coke deposit forming a chemical trap for the corrosive sulfur.

Deposition of coke and similar formations on surfaces depends not only upon the temperatures of decomposition, but also upon the chemical nature of the contacting metal and the physical nature of the surface of the metal. It would, therefore, be desirable to investigate the nature of the metals and surfaces upon which coke does and does not deposit. The nature of the metal is the most important factor.

For example, a highly-carbonized metal surface is more resistant to deposits in general, and also is closer in texture. An investigation, therefore, of interior carburized tubes would suggest itself.

COMPOSITION OF THE METAL

In the general discussion of corrosion it has been shown how the application of fundamental chemical and metallurgical principles may be used as a guide in the selection of metals and also in experimental work in the suppression of corrosion.

Keeping in view the questions of mechanical strength and economy of capital cost of plant, the basic material of construction has been mild steel. This has been alloyed with various elements such as chromium and aluminum. The high resisting qualities of aluminum to sulfur attack are well known to refiners; and, therefore, a close study of the related elements would be of value. The element titanium—which has been given third place in the series aluminum, chromium, titanium—would indicate the desirability of a concentrated study of titanium steels.

Perhaps more important is the study of the silicon alloys. If a method can be found of impregnating the surface of a strong carbon steel with silicon, thus combining the highly-corrosion-resistant silicon alloys with a backing of strong metal, a widely useful material would be in the hands of the refining industry. The possible low price of such a volume product would enable it to be used in the high-temperature and low-temperature parts of the plant, and it offers the solution of many phases of the corrosion problem.

Since the writing of the above paragraph, a process has been found to accomplish the impregnation of steel with silicon. Bubble caps and tubes up to 6 feet long are being tried out, and the results will be watched with interest.

LOW-TEMPERATURE CORROSION IN PRESENCE OF WATER—ELECTROLYTIC CORROSION

This type of corrosion is found in those sections of the plant where water may be condensed and form a vehicle to carry the corrosive acids, salts or dissolved gases.

These sections are the partial condensers, submerged-coil condensers, after coolers, and run-down lines.

This form of corrosion has been explained in modern times under what is known as the electrolytic theory of corrosion. It is essentially based upon the fact that an electrolytic cell is formed between the various metals used in the construction; or between the metallographic phases of the metal; or between the metal and the corrosion products in presence of water containing salts. These factors are again influenced, as discussed later, by the concentration of the salts in the water (called electrolyte) and oxygen concentration. An oxygen-concentration cell may be formed between different parts of a single phase of a pure metal, set up by the difference in oxygen concentration at two points in the "circuit" and other factors.

CONTROLLING FACTORS

Probably the most important point in connection with the question of corrosion has been the discovery of what is known as the "controlling factor." In this conception it has been found that there is a principal factor controlling the rate of corrosion, and underlying this there are other factors capable of considerable variation without influencing the rate of corrosion.

SOLUTION PRESSURE

When dealing with large quantities of condensate as in any commercial condensing system, the primary factor is probably the solution pressure of the metal. If, for example, iron as a single phase corrodes or dissolves at a certain rate in dilute acid, it is possible, by the addition of other elements to the iron, to lower the solution pressure and thereby reduce the energy dissipated in the form of corrosion. For example, the solution pressure of iron may be reduced by the addition of 14 to 20 percent of silicon. Also the solution pressure of zinc-copper alloys may be reduced by the addition of tin, which forms a solid solution in the alloy and tends to reduce its solution pressure. Tin in excess of the quantity soluble in the zinc-copper alloy has an important bearing on corrosion—which is discussed later.

The energy lost in the form of dissolved metal is the important factor. This energy may be expressed by the old equation $E = mv^2$ (where E represents the energy, m the mass, and v the velocity of the

mass m) which has become famous in its application by Einstein to the problem of light. He was careful to put into his equation the correct physical factors, and so achieved world-renowned results. The same conception may be applied in the first instance to the problem of corrosion in refineries. It is not desirable to reduce the velocity or the mass of condensate passing over the metal. In fact, it is necessary to accelerate the velocity and increase the mass for the purpose of maximum heat transfer and for the purpose of maximum heat transfer with the available pressure drop and economical friction losses. The addition of chromium to iron results in an alloy of high heat-resisting qualities and high creep strength with a lower solution pressure. In order, therefore, to avoid the loss of energy in the form of corrosion, the solution pressure of the metal must be reduced or the character of the dissolving agent altered by neutralization.

What methods have been tried to effect this reduction of solution pressure? Two methods have been mentioned for the copper-zinc alloys. For the iron alloys there is the addition of silicon, the addition of chromium, and the reduction of the carbon content.

The reduction of the carbon content is advisable on account of its tendency to segregate. It has been shown by Bain, Aborn, and Rutherford[8] that, at high temperatures in the absence of stabilizers, there is a tendency for carbon to separate at the crystal boundaries—which results in a loss of strength. Also, some of the worst examples of corrosion in steel plating in a continuously-flowing electrolyte have been shown to be due to electrolytic cells set up by the segregation of carbon into areas which become cathodic to the lower-carbon-content areas of the plate. Probably less attention has been given to this question of segregation in steel plates than in the case of condenser tubes, which are more or less readily withdrawn and handed over for investigation; hence, the relatively large volume of work published upon the commercially lesser important question. The matter is now receiving the attention of the steel mills on high-tension steel plates.

The reduction of carbon content in the chromium alloys has, however, not been done for the above reason only, but for the advantage gained in raising the elastic limit of the steel while at the same time improving its workability at the expense of higher ultimate strength and other reasons. High-elastic-limit steels have enabled constructors to reduce sections of metal and consequent weight and capital cost very considerably. At the same time it has assisted in the suppression of corrosion by the elimination of carbon segregation, the reduction of solution pressure directly, or by the formation of protective films.

PHASES OF METAL PRESENT

In any commercial metal encountered in construction it is rare to find just one single phase. Some workers have endeavored to produce metals of one single phase to suppress corrosion, as, for example, the production of the single phase β alloy of copper and zinc for impellers of pumps, etc. But it is unusual to find a metal as a single phase; and, therefore, we have to consider the problem as it presents itself in the average commercial metal.

The segregation of carbon in steel, producing two phases which form an electrolytic cell in the presence of the electrolyte, has been mentioned. It functions in two ways to produce corrosion cells:

1. By segregation of carbon, resulting in regions of low-carbon ferrite and higher-carbon pearlite.
2. In the case of iron-chromium alloys, a depleted chromium region at the grain boundaries due to the formation of chromium-rich carbide.

Perhaps the most familiar case met with in the refining industry, viz., cast iron, may be taken as the basis for our discussion—although its use is limited to cases where its nature makes it suitable.

In cast iron three phases separate during the cooling of a casting, viz., graphite, cementite, and ferrite. When in contact with an electrolyte, such as dilute hydrochloric acid or acid cooling water, there is an electrolytic cell formed between the graphite and the cementite, and between the graphite and the ferrite—the energy or rate at which the corrosion of the soluble or anode part of the cell dissolves depending upon the solution pressure of the ferrite and cementite, and also upon the concentration of the acid or electrolyte and other factors.

The solution pressure may be lowered by the addition of other elevents to the metal. Also, the formation of two phases may be suppressed. In the case of cast-iron pipe, this can be accomplished to a considerable extent by centrifugally casting the pipe. As cast, this is in practically a single phase of cementite which, on annealing to give the pipe strength, breaks down into a finely-divided and well-distributed graphite and cementite. Thus the area of carbon or cathode surface is reduced, with consequent reduction in the rate of corrosion. More complete examples of this kind will be given later.

CONCENTRATION OF THE ELECTROLYTE—ACIDITY AND ALKALINITY

As is well known, the concentration of the acid or electrolyte influences the rate of corrosion, as, for instance, the fact that when the acid in an automobile battery becomes through any cause weak, the battery will not function adequately. The chemist has devised a quantitative means of indicating the acidity or alkalinity of a solution.

The acidity or alkalinity is stated in terms of the hydrogen-ion concentration. Thus, when hydrochloric acid is mixed with water, it is hydrolyzed into two "ions": a hydrogen ion and a chlorine ion. The concentration is measured in terms of the grams of hydrogen ion per liter of solution. The logarithm of the reciprocal of this number is called the pH value and is, therefore, stated as:

$$\text{pH} = \log \frac{1}{\text{hydrogen-ion concentration}}$$

Since the molecule of water is ionized in its own solution, the degree of hydrogen-ion concentration in a neutral water has been determined and found to have the value $\text{pH} = 7$.

In alkaline solutions the pH value ordinarily varies from 7 to 14.

In acid solutions the pH value ordinarily varies from 0 to 7.

Thus rapid corrosion may occur in strongly-acid or in strongly-alkaline solutions, examples of which in the refining process are corrosion of iron condenser tubes by hydrochloric-acid condensate and corrosion of brass condenser tubes by the dilute hydrochloric acid formed in the distillation of the crude, by reason of chlorides in

water present in all crudes, and by excess of ammonia added as neutralizer. This accounts for the differences noted in the corrosion reports; some are changing condensers from admiralty metal back to steel, or a patented steel; while others are changing back from steel to admiralty metal, or propose to make or are making "trials."

The need for limiting the conditions under which one or the other material will be successful, and the consequent difficulty of stating what metal any particular part of the plant shall be constructed of, before one knows the details of the working process used, is at once obvious.

INFLUENCE OF OXYGEN AND MOISTURE

In oxygenated salt solutions, such as chlorides, the corrosion is largely controlled by the rate at which oxygen can diffuse or is carried by a flowing electrolyte to the cathodic areas to depolarize the cell. The familiar dry Leclanche cell, broken open after use, shows the carbon rod at the center surrounded by black oxide of manganese, which oxidizes the hydrogen liberated at the carbon cathode. The depolarizing action is slow, and a flash-light battery after over-use will recover on allowing it to stand. This has been improved upon in recent times by allowing air to breathe into a porous carbon, resulting in a steady high-current battery for people in isolated areas. How does this affect the refiner? In a condenser using, say river water, acid in character, the amount of air circulated in dissolved form influences the rate of corrosion. In some of the corrosion reports, for example, reduction of condenser corrosion is obtained by re-circulating condensed water in preference to river water, but oxygen is again dissolved at the cooling towers or spray ponds; both the absence of salts and of tower-dissolved and entrained oxygen are important factors. In the case of impeller pumps, the dissolved oxygen is carried rapidly to the cathodic areas; hence the rapid corrosion of high-speed impellers, in which large volumes of oxygen are carried to the cathodic areas, causing rapid rise of the corrosion with increasing speed of the impeller.

On the other hand, it has been shown that in the case of steel with high concentrations of oxygen present in the electrolyte the corrosion is independent of the amount of oxygen present — the "controlling factor" there being the impurities or phases present in the metal.

In atmospheric corrosion which is met with in pipe lines laid near the surface or supported in the atmosphere around the plant, the "controlling factor" is associated with the corrosion products. To take a familiar example—a current is produced when a plate of oxide of lead is connected through an electrolyte to a spongy lead plate, and similarly, the corrosion product of iron in the atmosphere or damp soil will form a cell with the remaining iron. The activity of the cell varies with the humidity of the atmosphere and its contents (such as sulfuric acid). Thus in a concrete case one refiner reports that his plant pipe lines lasted 5½ years in the earth. Subsequent lines were carried above-ground. By so doing the corrosion cells were lessened, as the moisture-retaining character of the earth maintained a moist electrolyte in contact with these service lines to a much greater degree than given by the humidity of the atmosphere; hence, an increased life resulted for these pipe lines.

The principle of differential aeration also underlies certain types of corrosion. For example, a single-phase metal (one part of which is screened from access to oxygen) in contact through an electrolyte with another part, which has free access to oxygen, forms an electrolytic oxygen-concentration cell. Similarly, a corrosion cell may be set up by varying concentrations of the electrolyte at different points of the same metal, both cases being known as concentration cells.

INFLUENCE OF TEMPERATURE

The chemical action of corrosion which is being considered may express itself in the form of heat or as electrical energy, and the corrosion has been broadly classified on this basis.

The mathematical mind likes to express these things by using symbols to form a picture in the mind to facilitate thought. It has been shown that, if the electrical energy E is expressed in volts and the heat Q in calories:

$$E = \frac{-JQ}{nF} + \frac{T\,dE}{dT}$$

where J is the electrical equivalent of heat = 4.182 ergs per gram.

n = the number of equivalents of metal involved.

F = Faraday = 96,500 coulombs = 26.8 ampere hours.

Thus when $\frac{dE}{dT}$ is positive, the electromotive force of the cell rises with increase of temperature T. When zero, the electrical energy is equal to the chemical energy.

The familiar fact shown mathematically above is illustrated when trying to start an automobile on a cold morning. The lower temperature has affected not only the volatilization of the gasoline and increased the viscosity of the lubricant, but has also reduced the activity of the cell or storage battery.

The vapor or hot entrance end of condensers is, considering the water side only, subject to more rapid corrosion, generally speaking, than the exit end. Provided the electrolyte is not dried up, the corrosion increases with increased temperature. The higher corrosion rate of condensers using river water at unusually high temperatures has been mentioned in some of the corrosion reports sent in. On the vapor side of the condenser the direct corrosion is also more rapid where the hot vapors enter.

INFLUENCE OF PRESSURE

Pressure has been shown above to have great influence on high-temperature corrosion, but for low-temperature corrosion its influence is less marked. The case of gas-concentration cells is the only one likely to be of importance where increased pressure gives a higher concentration of the solution of the corroding gas; but as pressures are usualy low in the low-temperature section of the plant, it need only be considered insofar as it influences the solubility of oxygen in the electrolyte.

INFLUENCE OF EROSION

Much confusion has arisen in connection with the question of corrosion by lack of understanding on the related question of erosion.

Its influence may be useful in some cases and harmful in others. Where the initial corrosion sets up a protective film which is insoluble in the corroding liquid, the corrosion is reduced in amount—depending upon:

1. The electro-negative character of the corrosion product.
2. The direct permeability of the corrosion product or its ability to oppose diffusion of oxidizing gases.

3. Its osmotic membrane characteristics bringing into action concentration cells, thus varying the concentration of the electrolyte or corroding solution at various points on a single-phase metal.

The action of erosion generally is to increase the corrosive action by maintaining the primary corrosion conditions, since it mechanically removes the corrosion product and also brings up, in consequence, greater quantities of depolarizing oxygen to the cathodic portion of the corrosion cell. This effect, however, is to a very large extent dependent also on the solubility of the corrosion product in the electrolyte.

One of the most remarkable factors brought out in corrosion investigations has been the tenacity of the corrosion product, in dilute sea-water electrolytes, for example. Even when propellers have been run at cavitation speeds, the corrosion products may still adhere. In the refinery, however, the concentrations of the electrolyte are relatively high, and the corrosion products rapidly dissolve and are carried away by solution as distinct from the mechanical effect. Hence, we get erosion channels primarily due to variations in the metal, frequently assigned to mechanical erosion, whereas they are essentially corrosion effects.

The corrosion of turbine blading may be instanced as a typical case. With super-heated dry steam entering the turbines as a freely-flowing gas, free from all solid eroding particles, we get the blading "scored" as though mechanical forces were in operation. A change of material of the turbine blading to one of lower solution pressure has largely eliminated this. A further example occurs in impellers. The loss of metal has been attributed to erosion; and, when reaching cavitation speeds, the subject has been submitted to the mathematicians for elucidation. On the assumption that a cavity in the region of an impeller is a vacuum, it can be shown that an enormous blow will be inflicted if the cavity collapses instantly. As most impellers run in liquids containing much dissolved gas, and also as the liquid has an appreciable vapor pressure, the possibility of erosion by the sudden collapse of vortex cavities is quite improbable.

Since erosion depends upon mechanical action, the nature of the forces operating may be studied. Where the surface of the particle of corrosion product is large compared with its mass, it will tend to float. It is this type of erosion that the civil engineer has to contend with. In the refinery, however, the speed of flow tends to carry away the corrosion products only insofar as they are not dissolved in the flowing liquid. Most corrosion products, however, when deposited from solution are soft and have little, if any, abrasive power.

The erosion then may be considered to be due to the action of drops of the liquid striking the metal as, say at the entrance to a condensing tower. The force with which the drops strike the metal may be expressed as $F = Ma$; i.e., the mass multiplied by the acceleration or, in this case, the deceleration, as the drops of liquid are being stopped by the plate.

Acceleration or deceleration is expressed in terms of velocity change per unit of time, and velocity is distance covered in a unit of time. Therefore, the equation may be written $F = mv.^2$

The velocity of the drops of water, therefore, striking the plate would have enormous force if the change of velocity is from a high figure to zero in an *infinitely short time*. The time, however, is lengthened by the distortion of the drops as they strike the plate and other factors, and hence, the magnitude of the force is actually very small. The force has been found experimentally to be insufficient to wash away the soft corrosion particles when the vortex cavities formed in impellers are allowed to collapse. If the strength of the reacting solution is raised to the chemical solubility strength, the corrosion products are removed, and a fresh surface exposed continually to the attack of the corroding liquid. The corrosion then becomes a function of the mass of the reacting liquid passing the plate in a given time. As the mass or the number of drops of liquid striking or passing over the plate is proportional to the velocity, the erroneous idea has crept into the question that the action is mechanical erosion; whereas, as shown, it is primarily chemical corrosion.

This applies to turbines, impellers, pipe lines, and condensers where large volumes of corrosive fluid are continually passing over the surface of the metals. It has also been found that softer metals may be substituted with success in cases of so-called erosion, due to the fact that their solution pressure is lower—further showing that the problem is primarily chemical, and not mechanical.

One of the corrosion reports gives an example illustrating this question in the refinery. In this instance the impeller-pump return bends made of cast iron had an average life of two months. Machinable cast iron has a Brinell hardness of 180-220. The report comments: "we should replace with lead pipe." This has a Brinell hardness much below 100, but an entirely different solution pressure in the corrosive agent.

Another corrosion report gave a case of a centrifugal pump using a bronze impeller, handling alkaline and plumbite gasoline, where considerable pitting occurred and the impeller only lasted six months. A cast-iron impeller with a lower solution pressure in alkaline media was substituted, with the result that no further trouble was experienced.

This example is illustrated in other parts of the plant, by other reports, where the solution pressure of bronzes in alkaline liquids is high and the substitution of iron with a lower solution pressure results in decreased loss by corrosion.

The general conclusions regarding low-temperature corrosion may be summarized briefly:

Low-temperature corrosion occurs in parts of the plant where water condenses and dissolves acids and salts to form an electrolyte.

The electrolyte may attack the metal directly, or may set up electrolytic corrosion cells:

The direct attack of the electrolyte on the metal may be reduced by using metals of low-solution potential.

Electrolytic corrosion is caused by the presence of different metals or different phases of the same metal forming electrolytic cells with the electrolyte.

Electrolytic corrosion may be reduced by using single-phase metals of low-solution potential.

Controlling factors may influence the rate of electrolytic corrosion. These factors are: concentration of the electrolyte; solution pressure of the metal; presence of extreme electro-positive and electro-negative phases of metal; oxygen concentration in the electrolyte; movement of the electrolyte and temperature of the electrolyte.

PROTECTIVE METHODS FOR COMBATING LOW-TEMPERATURE OR ELECTROLYTIC CORROSION

The methods available for the protection of the metal against electrolytic corrosion may be conveniently classified for the purpose of clarity, as follows:

Methods Involving Composition of the Metal.

a. Methods which utilize metals of low electrode potential.
b. Methods which suppress the formation of electrolytic cells by using single-phase metals when commercially possible.
c. Methods in which electrolytic cells are deliberately produced (with the object of distributing the corrosion over as large an area as possible).

Methods Involving the Formation of an Electrolytic Cell in the Plant by Means of

a. A protective metal which is subject to the whole corrosion.
b. The formation of an electrolytic cell in the plant by the application of electric current from external sources.

Chemical Methods Using Added Chemical Agents as Neutralizers

METHODS INVOLVING THE COMPOSITION OF THE METAL

a. Methods Which Utilize Metals of Low-Electrode Potential

In the high-temperature portions of the plant it was considered desirable to use the metal which reacted with the greatest difficulty with the corrosive agents; so also, in the low-temperature sections, the least reactive metal is chosen consistent with mechanical strength requirements.

The best guide in this connection is the electrode potential of the metal. This is usually measured against a standard or calomel electrode, which consists of mercury in a solution of calomel (mercurous chloride). The glass vessel in which the electrode is built is fitted with a side tube, so that it may dip into the electrolyte in another vessel containing the metal whose potential is to be measured.

For comparison purposes, the hydrogen—hydrogen-ion electrode is used, and the figures given in Table 4 are for this electrode as zero.

TABLE 4

Metal	Electrode Potential (Volts)
Aluminum	+1.7
Manganese	+1.1
Zinc	+0.758
Chromium	+0.6
Iron	+0.5
Nickel	+0.22
Tin	+0.13
Lead	+0.12
Hydrogen	0.000
Bismuth	—0.2
Copper	—0.51

The practical application of these electrode-potential values to the question of lowering the solution potential of metals used in the low-temperature sections of the refinery can be seen in one or two examples.

Boiler plate or shell steel is a widely-used material in the refining industry. By the addition of copper its corrosion-resisting properties are improved, as is well known. Unfortunately, the solubility of copper in iron to form a complete solid solution is small—of the order of ½ percent when the metal is slowly cooled—although at 1100°C. the solubility is said to be 3 percent.[9] If larger amounts of copper are added, the excess above what will dissolve separates out as a second phase. The action of this second phase of metal will be considered later.

Another example, which has been in practical use by locomotive engineers for many years, is the addition of arsenic, and many locomotive boiler-plate specifications call for additions of arsenic.

Phosphorus is another element which acts in a similar manner; and, where strength factors make it tolerable, it is used in practice. When the percentage used is below the solubility factor and suitable heat treatment is given, phosphorus is useful in suppressing corrosion. Bismuth has also been used to lower the solution potential, but its low solubility and mechanical characteristics generally preclude its use. Several of the corrosion reports have indicated the success of this method of protecting from excessive corrosion by lowering the solution potential of the metal, particularly in the use of the copper steels.

b. Methods Which Suppress the Formation of Electrolytic Cells by Using Single-Phase Metals

Assuming that the metal with the lowest solution potential has been chosen for any particular part of the plant, it is evident that the depth of penetration will be less if the area exposed to the electro-chemical action is relatively large, and also if there are no other phases of metal present which will form electrolytic cells with the main body of metal.

Thus, in lowering the solution potential of steel by the method discussed under (a), it is essential that the added element shall not separate out to form other phases which would set up electrolytic cells. As an example: the amount of copper added to steel for the purpose of lowering its solution potential must not be greater than that which will remain in solution when the steel is slowly cooled. If an excess is added, then it separates and forms cathodic areas which accelerate the corrosion of the main body of the steel. The amount of copper which separates is influenced by the heat treatment of the steel, and the principle of rapid cooling is used in the heat treatment of some alloys to prevent the formation of more than one phase. With soft steels, such as boiler plate, annealing followed by slow cooling is usually the final operation; and, therefore, there is a great tendency for the dissolved metal to separate when its solubility is lower in the cold state than in the hot state. The application of this principle in practice is, however, shown in the suppression of segregation by the rapid cooling of the chromium steels—thus preventing the separation of chromium carbides with, in addition, depletion of the chromium content in those regions near the place of carbide separation.

Some of the most useful single-phase alloys used in the refining industry are the *a* brasses. These alloys of copper with zinc up to 30 percent form a single-phase or solid solution known as *a* brass. The solution pressure of this single-phase alloy can be lowered by the addition of other elements as, for example, nickel and tin. Hence, the makers of condenser and heater exchanger tubes submit for use *a* brass tubes in which various percentages of tin or nickel are alloyed. Probably the most satisfactory alloys, when considered from this angle, are the *a* brasses with nickel added—since nickel is more soluble in the alloy than tin. Probably in this connection a useful research would be to determine the maximum solubility of nickel and of tin in the *a* brasses. The copper-nickel alloys without zinc are the best, chemically and mechanically, but they are expensive. Another of the technically-useful single-phase alloys is the *a* bronze. In these alloys we have two low-electrode-potential metals forming a single phase and, hence, find that their corrosion resistance is higher than that of the *a*

brasses—which contain zinc, with its objectionable higher electrode potential. For ease in mechanical working and to assist in maintaining the tin in solution, small percentages of zinc are added. The corrosion reports show varying degrees of success in the use of these single-phase alloys due to several factors, some of which concern the metal and some its misapplication.

c. Methods in Which Electrolytic Cells Are Deliberately Produced

The object of this method of reducing corrosion is to distribute the corrosion over as large an area of metal as possible, and so reduce the depth of penetration.

Several examples of the application of this principle to the refinery plant may be usefully considered. The problem of riveting presents considerable trouble as recorded in the corrosion reports. In some cases the corrosion of the rivets is excessive, and in others the corrosion of the plate is around the rivets. Here a definite corrosion cell is set up according to the nature of the metal in the plate and in the rivet. Since riveting requires a rapidly-working metal, the tendency has been to use a low-carbon steel or a soft iron. With a lower carbon content than the plate, the rivet becomes anodic to the plate and corrodes away. This is modified to some extent by the work-hardening of the rivet. Where this rivet type of corrosion has occurred, some members have substituted copper-steel rivets with success. The tendency here is to throw the plate into the anodic condition to the rivet, and the plate corrodes. In practice, therefore, since the rivets are more easily replaced than the plates, the policy should be to work for an anodic rivet. If the composition of the rivets is the same as that of the plate, the strained metal due to riveting renders the rivet anodic; and, therefore, the rivets used should be slightly higher in carbon content than the plates, so that in the final condition the two will have the same electrolytic characteristics. In practice this is difficult to attain; as the amount of work put on the rivets is not known, nor have exact determinations been made upon the influence of work upon electrolytic potential.

Cases in which electrolytic cells are deliberately formed in the metal during the course of manufacture are of wide application. There are, for example, the bronzes in which tin is added to copper in excess above that which the copper will dissolve to form a solid solution. The excess of tin separates out as what is known as the δ phase. This phase is cathodic to the remainder of the alloy; and, therefore, the corrosion of the alloy is distributed over a large area. Since also the solid α phase of tin in copper has a comparatively low-electrode potential, the electromotive force set up in the case of the bronzes between the two phases is small, and the bronzes have a high reputation for their ability to resist corrosion.

Another example is found in the well-known admiralty metal used as exchanger and condenser tubes. Since the α phase of the copper-zince alloys has a fairly high electrode potential due to the presence of the zinc, tin is added for the double purpose of lowering the solution potential of the α phase and, also, it is added in excess—resulting in the formation of a second phase which, being cathodic to the main portion of the metal, results in the distribution of the corrosion over a wide area and, consequently, a lower depth of penetration.

The type of corrosion exhibited when this method of protection is used is of considerable interest. The corrosion is spread over a large area and, hence, appears to be lower. This is only true, however, insofar as the general solution potential has been lowered by the tin in solid solution. When the alloy corrodes, the zinc—having a high solution pressure—is dissolved, and leaves a network of copper of low mechanical strength. A similar case is seen when cast iron corrodes—the soft graphite being left behind, while the iron has gone into solution. These cases have become so well known as to merit special names, viz., dezincification and graphitization, respectively.

Lead is also frequently added to the copper-zinc alloys for the purpose of reducing corrosion. Its solubility in solid solution is not very great, and it is usually found at the boundaries of the α crystals.

Generally, in commercial alloys, all the above methods of suppressing corrosion are simultaneously operating. The alloys have been developed by the process of trial and error without an understanding of the fundamental factors underlying their operation and, hence, the varying claims as to their individual superiority.

Probably the most important method used technically for the suppression of corrosion along the lines discussed above [under (a), (b), and (c)] is the lowering of the solution potential by the addition of elements which remain in solid solution in the alloy. The reason for this is the fact that the solid solutions are generally more easily worked.

METHODS INVOLVING THE FORMATION OF AN ELECTROLYTIC CELL IN THE PLANT BY MEANS OF:

a. A Protective Metal Which Is Subject to the Whole Corrosion

This is an ideal method of controlling corrosion; but it is not successful to a great extent in practice, for reasons which are discussed later. The most important applications of this method have been in condensers and boilers.

The method consists in attaching, to the part to be protected, a highly-anodic material (usually zinc plates) which form an anode, the condenser tubes or boiler shell and tubes forming the cathode—thus being protected at the expense of solution of the zinc anode.

This method has been one of the most successful in practice where conditions are favorable. These conditions are a steadily-flowing electrolyte of weak character, free from excess of dissolved or entrained oxygen.

These conditions are only found in certain sections of the refinery plant, such as in the cooling-water side of condensers; and, hence, this method of protection is inapplicable to such parts of the plant as condensing towers and spray pipe condensers.

Its faults under good conditions may be considered. Good electrical contact between the zince plates and the part to be protected is essential. Commercially-pure zinc plates must be used, which are free from layers of segregated lead. In one case examined the plates lasted a few weeks, instead of many months in high-pressure boilers. On examination it was found that the zinc plates consisted of alternate layers of lead and zinc, which formed corrosion cells and rapidly consumed the plates without giving protection. Another fault of this method is that the protective current formed takes the path of least resistance, which is naturally the shortest distance between the anode and cathode, and so gives only a limited area of cathode protection. Hence, in some of the corrosion reports this method is stated to be useless.

b. The Formation of an Electrolytic Cell in the Plant by the Application of an External Electric Current From External Sources

This method has been patented and applied on a

fairly large scale. It is only applicable under the conditions given for (a) above and, hence, is only of limited application in the refinery.

Its faults are also those of the method (a), the chief being the short-circuit path which the current takes through the electrolyte giving only local protection.

In boilers this method is said to prevent scaling. This is accomplished by using a high-current density, such that hydrogen is liberated on the protected cathode surfaces, which liberation lifts the deposits of scale. If the temperatures and current densities used, however, are such that chlorine and chlorine oxides are generated, the results are disastrous. Further, the anodes used (usually iron bars) are converted into hydroxide of iron—which will cause priming, and also pass over into engines and turbines, with consequent trouble. It has also other and more serious disadvantages in certain situations, and should not be used without first obtaining expert advice.

Probably the most simple and, in suitable places, effective application of electrical methods of protection is afforded by the grounding of all parts of the plant to the negative pole of the generators. Thus, the tendency is brought about for all stray corrosive forces to flow toward the metal, the latter now being rendered cathodic. This method has been tried effectively on the small and large scale, although not generally known. Obviously, such a method of protection is only useful in cases where the corrosion energy is experienced electrically. It would be useless in protecting a fractionating tower, subject to the action of large volumes of hydrochloric acid.

CHEMICAL METHODS USING ADDED CHEMICAL AGENTS AS NEUTRALIZERS

This method is probably the simplest of application, and also the most effective method for protection against low-temperature corrosion in the refinery. This is confirmed by the corrosion reports.

The corrosive agents which reach the low-temperature section of the plant during the processing of the oil are:

1. Hydrochloric acid and chlorides
2. Hydrogen sulfide
3. Naphthenic acids
4. Carbon dioxide

together with quantities of sulfur and chlorides passing over mechanically and of corrosive products volatile in steam or carried over as dissociation products.

The neutralizers which are being used successfully are:

1. Gaseous ammonia
2. Ammonium hydroxide
3. Caustic soda
4. Soda ash.

1. Gaseous Ammonia and Ammonium Hydroxide

These are probably the most desirable low-temperature neutralizers with the majority of crudes.

The first cost of injection equipment is low, the control simple, and the handling hazards small. Good contact is easily obtained between the neutralizer and the large mass of material being handled. The products of neutralization, viz., salts of ammonia, are readily soluble in water and, hence, do not give the trouble which has been experienced in some cases when using caustic soda.

The chief danger lies in the use of an excess of neutralizer where the condensers are made of copper-zinc alloys, these being subject to corrosion by alkali.

One refiner, however, reports that, even when injecting ammonia into the cold crude to an excess of 500 percent over the theoretical requirements for neutralization, there was no corrosion of admiralty metal equipment. Its use in this manner for the high-temperature sections of the plant is of doubtful benefit. It tends, however, to render the corrosion more uniform.

Analysis of the corrosion reports shows that various degrees of neutralization are being used, the pH value of the distillates varying from 4.5 to 8. Table 5 summarizes the results reported.

These results show satisfactory evidence of the value of ammonia as a low-temperature neutralizer. As regards direct cost, it is the most expensive of the low-temperature neutralizers. On the basis of neutralizing value, its cost is approximately the same as that of caustic soda. On account, however, of the unstable character of the neutralization product—ammonium hydrogen sulfide — a larger excess of ammonia is required than is the case with caustic soda, which tends to increase the cost of application of ammonia.

2. Caustic Soda

This neutralizer has certain distinct advantages and disadvantages when compared with ammonia.

It forms more stable compounds with hydrochloric acid, hydrogen sulfide, and the naphthenic acids. The ammonium compounds are more readily dissociated than the sodium compounds. Caustic soda is, therefore, particularly useful as a neutralizer when large volumes of hydrogen sulfide or large quantities of the naphthenic acids have to be handled.

The corrosion reports show that it is, therefore, in great favor in the handling of California crudes; since, if present in sufficient quantity, it removes hydrogen sulfide from the distillate.

When a pH value of 8 is maintained in the condensate, corrosion is stated to be practically eliminated in low-temperature parts of the plant.

One member reported that continuous operation of the plant would be impossible without the use of caustic soda—since partial condensers, condensers, and coolers rapidly failed by corrosion.

The quantity used by members varies from 0.004 to 1.1 pounds per barrel treated, the latter figure being exceptional. The majority show figures varying between 0.004 to 0.4 per barrel of condensate.

One member reports that with 0.02 pound of caustic soda per barrel, and a pH value of 8, no corrosion occurred; but hydrogen-sulfide gas was present in the gasoline. When using 0.06 pound of caustic soda per barrel, there was no need to doctor the distillate. It was conservatively estimated that caustic soda saved $250,000 per year in addition to the corrosion saving, which could not be evaluated.

The chief danger in the use of caustic soda is, as it affects the plant, by causing caustic embrittlement of the steel. Caustic embrittlement has been discussed under high-temperature corrosion, but its action under low-temperature conditions is not likely to present difficulties if adequate control of excess addition is exercised. Caustic soda is also stated by some members to be disadvantageous where the residuum is being worked for asphalt.

The method of application is by means of an aqueous solution of 15° to 25° Baume strength. It has been

TABLE 5

Low-Temperature Ammonia Neutralization

Refiner	OIL PROCESSED	Ammonia (Lb. per Bbl.)	pH of Value Condensate	Effect on Low-Temperature Corrosion
2	Mid-Continent crude	0.0155	7+	Slowed down considerably
3	Mixture of crudes	0.02	7+	Practically inhibited
6	Mid-Continent crude	0.009	7.5	Reduced 95 percent
7	Crude oil	0.0028	6.8	Not evaluated
8	Panhandle-Kansas crude	0.001–0.002	Probably less than 4.5	Reduced 25 to 50 percent
8	Crude oil	0.0025	Probably less than 4.5	Only slightly reduced
9	Gulf crudes	0.01	4.5+	Practically eliminated
10	Texas crudes	0.0025	About 7	Reduced to a minimum
14	Kansas crudes	0.0054	.....	Reduced
16	California crudes	0.003	4.5 to 8	Being controlled
7	Cut-back residuum	0.266	6–8	Not evaluated
16	Pressure distillate	0.05	4.5–8	Being controlled

found essential in order to obtain adequate mixing that the caustic soda be sprayed into the line; in consequence of which it is necessary to filter the caustic-soda solution to free it from calcium carbonate and magnesium carbonate which plug the sprays. This is accomplished by filtering through sand filters.

3. Soda Ash

This has no useful advantage over caustic soda, being a weaker alkali and less effective than either caustic soda or ammonia. In one instance it was reported to have given less alkali corrosion of admiralty metal tubes than was the case when using caustic soda. It is less expensive than caustic soda when based upon the equivalent neutralizing power. In handling large volumes of hydrogen sulfide or sulfur it is not so useful as caustic soda and, hence, has not been used in many refineries.

The three neutralizers discussed have each been applied successfully. Ammonia is the most expensive, but has technical advantages which offset the higher cost.

Caustic soda is generally more effective, since it gives a higher hydroxyl-ion concentration; and a preference for either depends upon factors outside the chemical question of neutralization, such as handling and transportation.

RECOMMENDATIONS FOR LINES OF INVESTIGATION

The problem of the suppression of low-temperature and electrolytic corrosion probably covers a wider field than the problem of high-temperature corrosion. Recommendations for lines of investigation may be conveniently considered under the following divisions:

1. Process
2. Modifications of Plant
3. Composition of Metals.

PROCESS

Under the question of the process the use of neutralizers should be considered. The use of a neutralizer represents a fundamental change in the process, and may consequently involve a modification of the plant.

The simplest and most direct mode of attacking low-temperature corrosion appears to be along the lines of finding the best neutralizer to use, consistent with economy. A considerable amount of successful work has already been done, as reported in the corrosion reports.

NEUTRALIZERS OTHER THAN THE COMMON ALKALIS

Certain neutralizers, other than those extensively reported in the corrosion reports, are capable not only of neutralizing the acid present in the condensates, but also of reacting with the metal to form a protective coating. Probably the most important of these is sodium hydrogen phosphate.

Mention of a trial of this neutralizer has been made in one report. The probable reactions taking place are:

$$Na_2HPO_4 + 2HCl = 2\,NaCl + H_3PO_4$$
$$2\,H_3PO_4 + 3\,Fe = Fe_3(PO_4)_2 + 3\,H_2$$

The latter reaction is used in a patented process for the formation of a protective film on the surface of steel to prevent rusting. The possibility of forming this highly-adherent iron-phosphate film on the surface of the steel, in presence of neutralizers, may repay study.

If, on the other hand, the phosphoric acid passes through the plant after neutralization of the hydrochloric acid, its corrosive effect is lower than that of hydrochloric acid—and it may be neutralized, after separation in the aqueous condensate, with caustic soda and the sodium hydrogen phosphate formed used over again.

The hydrogen sulfide would also probably be ab-

TABLE 6

Low-Temperature Neutralization by Caustic Soda

Refiner	OIL PROCESSED	Caustic Soda (Lb. per Bbl.)	pH Value of Condensate	Effect on Corrosion	Improvement of Distillate
7	Crude oil	1.1	8	Not evaluated	Not evaluated
8	Kansas crude	0.058	H_2S free	Reduced considerably	Gasolines use less plumbite to sweeten, and color stability greater
8	Dubbs operation	0.1	H_2S free	Reduced 50–75 percent	.....
8	Cross operation	0.005	H_2S and SO_2 free	Reduced 50–75 percent	.....
8	Re-running pressure distillate	0.027	About 4–7	Reduced 50–75 percent	.....
15	California crudes	0.01–0.02	About 7	Life of equipment extended 4 to 10 years	No improvement in quality
16	California crudes	0.02	About 7	Not evaluated	Distillate improved in color, and corrosion controlled
16	Distillation of pressure distillate	0.3	About 7	Not evaluated	.....
16	California crude	0.004–0.01	About 8	Not evaluated	Some improvement in color
16	Cracking	0.09–0.15	About 8	Not evaluated	.....
17	California crude	0.04–0.06	H_2S free; about 8	Practically inhibited	All sour and corrosive sulfur removed and color improved
7	California naphtha	0.04	About 8	Practically inhibited	No change

sorbed, judging from a cursory examination of the heat balance in dilute solution, according to the equation:

$$Na_2HPO_4 + H_2S = NaHS + NaH_2PO_4$$

a study of sodium hydrogen phosphate as a neutralizer would, therefore, appear to be a worthwhile investigation.

MODIFICATIONS OF PLANT

a. The possibility of separating the hydrochloric acid and hydrogen sulfide before condensation of the petroleum vapor also offers problems for investigations of plant modification in relation to suppression of corrosion.

Where the corrosion problem is unusually acute, an investigation into the use of neutral or acid brick-lined jet condensers — carrying the alkali for neutralization through sprays, with subsequent separation of the aqueous portion and re-heating the petroleum fraction for rectification — would be worth consideration. It would, of course, necessitate closed-circuit working.

The subject has been partly attacked by experimental work on non-metallic linings for the upper parts of fractionating towers, but in most chemical processes the economical method is to conduct each operation in an especially-designed section of the plant.

b. Modifications of the refinery have been made with respect to metals as, for example, the substitution of steel for admiralty metal in condensers when ammonia has been used as a neutralizer. It is evident, from the corrosion reports, that there is no definite opinion as to the necessity or otherwise for these minor changes. Investigations would, therefore, be desirable in order to advise refiners as to the limits of excess of alkali permissible in contact with the various copper alloys in use. This would take the form of a pH-value relation to depth of penetration for each alloy.

c. The application of protective films to the metal for purposes of protection against low-temperature corrosion is worthy of investigation.

The major difficulty has been in obtaining permanent contact with the metal. The adhesion of oil paints to surfaces has made them of wide application in atmospheric corrosion, but these films are useless in the case of interiors of plants. Under the subject of high-temperature corrosion, the applications of plated metals were discussed. The possibility of applying plating to the interior surfaces of low-temperature equipment should not be overlooked. For a long time past tin-coated condenser tubes have been available commercially, and other coatings or platings are possible. Tin coatings, however, have not been successful with high percentages of hydrochloric acid. The chief difficulty lies in the adhesion of the enamel to the steel under conditions of fabrication and use. It should, however, be possible to find an enamel with a suitable coefficient of expansion capable of surfacing the interior of the plant, and with satisfactory adhesion and good mechanical properties—given time and facilities for the investigation which are essential to the solution of any problem. Studies have been made elsewhere on the application of enamels, *in situ*, to pipe lines for the purpose of suppressing corrosion; and these have had a moderate degree of success, in view of the limited time devoted to the problem. Such enamels would have a wide field of application in the whole petroleum industry, as well as in the refinery.

The general tendency noted from the corrosion reports is to regard the solution of the low-temperature corrosion problem as mainly a question of the correct composition of the metal. This is only true after all other methods of attack have failed, since the return of the metal to its natural state of combination with other elements is the vital factor that the refiner is combating.

The search for a metal which will meet the requirements of great resistance to low-temperature corrosion covers a wide field, and there are several angles from which it may be attacked. Low-temperature corrosion has been shown to be both mass chemical action and electrolytic corrosion. Both would be met by the ideal metal, insoluble in acids and alkalies, with no solution potential, and existing in one phase. The only metal approaching this ideal is platinum, which is prohibitive economically.

If copper alloys are considered essential to the industry, they should be concentrated on from the metallurgical angle in regard to the production of low-solution-pressure solid solutions of workable character.

Consideration of the chemical characteristics would indicate that the copper-nickel, copper-cobalt, cobalt-titanium solid solutions, and combinations of these would be worthy of study.

Caution is essential in making tests of metals in the plant. For example, the insertion of a length of special alloy pipe in a line of other metals is not a reliable way of testing a new metal for its corrosion qualities, as an electrolytic cell is set up frequently between the new metal and the old.

Probably steel is the best metal to use in a refinery where neutralization is practiced, and much investigation work on solid solutions of alloying elements in steel remains to be done. A close study of the figures given in the earlier parts of this publication will indicate the lines of attack.

High-percentage, expensive alloys are not always essential. For instance, in parts subject to alternating stress and abrasion, where 14-percent manganese steel was in use with daily failures, a substitution of a plain-carbon steel with suitable heat treatment resulted in an enormous saving to the producer and an entire elimination of fractured parts.

The essentials to progress of any investigation are not only an exact knowledge of the particular subject, but also an adequate knowledge of the correlated subjects. For example, a metallurgist may know the advantages of nickel in steel as regards its toughening qualities, but how many of them know its limitations in the machine shop when running on mass production of gears? Indications of its limitations in the refinery have been indicated in the discussion of high-temperature corrosion.

The need for an open mind is essential for the solution of all these problems. No doubt, the men of sail smiled when Fulton's steam kettle, in a boat, chugged past them on the Hudson a short one hundred years ago; but even he himself may not have visualized the "Queen Mary" crossing the Atlantic Ocean in a short four days.

The cost of corrosion in various industries has reached a very high figure, and in the refineries in the United States is estimated at $125,000,000 annually (W. L. Nelson, *Petroleum Refining Engineering*). Compared with mechanical or abrasive wear and tear, it is probably a much higher factor in the depreciation of all forms of plant. Considerable experience has been gained in combating it, and in the majority of cases the most economical and efficient method has been by the use of neutralizers.

All too frequently decisions are based upon capital cost alone, and comparisons of technical-economic ef-

ficiency of various improvements becomes difficult where the particular improvement is made to carry a high general overhead charge. For instance, the accountant, in considering the cost of material and labor for an improvement in a protective material for steel, rarely has available the high depreciation figure for the particular part of the plant subject to the improvement and increased life. The costs of an improved material for protecting steel — absolutely suppressing chloride corrosion—were less, in one case, than one half the cost of the old corrosive materials. The labor charge for application was a constant for both cases; but, the overhead of that particular plant being calculated 250 percent of the labor costs, the cost of production of the new protective material showed 1 cent less per square yard covered. Had the depreciation rates been added to the cost charges in each case, no doubt the economy would have shown a handsome return.

Frequent mention is made in the corrosion reports of the neglect to adopt, for example, a new metal for a valve on account of high capital cost of the new valve. This is not the most desirable viewpoint, since labor charges and general overhead would indicate that the only question to consider in such cases is the technical efficiency of the metal. The increase in the general overhead charges, to which the increased cost for special metals in a few valves is added, is almost negligible.

Where the corrosion is due to atmospheric or weak-acid attack (such as in the building, engineering, chemical, and refining industries) neutralization has proved itself to be the most economical method, in that it rarely involves high capital cost of application, is easily controlled, and demands comparatively low maintenance charges.

Where applicable to building structures, protection by means of alkaline concrete, such as in foundations, is most effective. Concrete has also been found effective in certain vessel interiors, discussed earlier herein.

Cement, which is the basis of concrete, is readily available in all parts of the country. It is easily handled, and its cost is comparatively low. Considerable work has been done in regard to making it available for thin surfacings; but the problem of adhesion of thin cement films has not yet been solved, although some success in this direction has been reported.

Economically, it is one of the cheapest protective agents available.

For structures where the mass application of concrete is not possible, it is necessary to fall back upon asphalt compositions. These are very efficient and economical if correctly manufactured. They have the essentials of a good protective agent, viz., efficient contact with the metal and imperviousness to the passage of moisture. Their disadvantage is in lack of abrasive resistance and the large number of inadequately-manufactured asphalt compositions upon the market. This latter factor has given them a bad reputation in some quarters, but of their essential efficiency and economy there can be no doubt.

The question of water for use in the refinery is deserving of consideration. The case most frequently occurring is that of acid waters. In this case the use of alkali for neutralization is the most economical method of treatment, if possible combined with atmospheric cooling and re-circulation. Followed by de-aeration and the addition of a small percentage of sodium chromate, continuous re-circulation is possible where the available water supply is limited.

Machinery (revolving and reciprocating parts handling corrosive liquids) requires consideration according to the nature of the corrosive liquid being handled. Where it is not economically possible to neutralize the corrosive liquid, or the nature of the process renders such method of attack impossible, it is necessary to fall back upon a metal capable of economically resisting the corrosive attack.

Each part of the machinery requires separate consideration. Piston rods and pump rods may be made, according to conditions, of either case-hardened steel or of forged manganese bronze. Castings may be made in high-silicon-alloy cast iron or high-chromium alloy steel. The surfaces of valves in frequent use are generally more economically made in high-chromium alloys, having regard to their economic length of life.

The chemical section of the refinery presents a variety of corrosion problems due to the extremely corrosive nature of the material handled, the chief of which are the oxygen-sulfur compounds.

A large variety of materials from fused silica to cast iron are available—and used according to concentrations of the acid and other circumstances—so that the best material to use economically depends upon the particular case. The corrosion reports deal with a large variety of cases. No hard and fast rules for general application can be laid down.

The distillation section of the refinery has been discussed fully from the technical point of view. Economically, the burden of the corrosion problem must be carried in the price of the products to the consumer. The particular crude to be processed may not be able to carry the cost of efficient technical plant for its processing, and such crudes may have to await marketing until such a time as prices of the finished products warrant their processing.

The corrosion reports indicate, in many cases, the economic feasibility of using special alloy equipment, due—other things being equal—to the increased length of running periods these alloys allow. There is also adequate evidence that the majority of crudes do not require expensive alloys in the distilling sections, but that further attention to improvements and application of acid-brick linings to condensing sections would be of economic advantage to the refiner. General improvements of this kind usually entail minor problems, but these latter should not suppress the desire for main-line progress.

The economic question of the distribution of the research burden between the steel producer and refiner is also a matter for consideration. For example, in one case, the substitution of a cobalt steel for a plain carbon steel resulted in a change in length of useful life from one month to more than 10 years. The price difference between the two steels cannot carry the resulting loss in tonnage to the steel manufacturer. There is no "yes" and "no" to the multitude of economic problems in the refinery. Each may be economically bridged; but, to use an analogy, whether the bridge be plain-suspension, cantilever-suspension, continuous-girder, or flexible-girder will always depend upon a variety of circumstances, and must be settled for each individual case.

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Motor Fuel *from* Catalytic Treatment of Cracked Gases

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WITH the automobile and airplane industries ...cing motors with higher compression ratios and greater speeds than ever before, the oil industry has produced the gasoline making it possible for these motors to function. The octane rating or fuel efficiency of gasoline has been in advance of engine design. The cracking process has contributed to the rising octanes not alone in the production of high anti-knock gasoline but also in furnishing cracked gases which can be catalytically converted into as high as 100-octane motor fuels.

Since 1925 the top speed of automobiles has increased from 60 to over 100 miles per hour, while cruising speed of airplanes has developed from 80 to 260 miles per hour, as shown by the 9-hour and 27-minute record-breaking California to New York flight made early this year, using 100-octane gasoline.

The catalytic polymerization process of the Universal Oil Products Company[1] is commercially operating. There are operating and under design or construction, units to produce about 430,000 gallons of polymer gasoline per day, or at a yearly rate of 157,000,000 gallons of 80-to 100-octane gasoline.

The new polymer gasolines have greater chemical uniformity than regular gasoline, since one is largely composed of olefin hydrocarbons and the other is made up of isoparaffin compounds, while regular gasoline is made up of paraffins, olefins, naphthenes, and aromatics in widely varying percentages. The oil industry is now in a position to furnish motor fuel with but few hydrocarbons present or even single hydrocarbons such as iso-octane, thus making it possible to control the combustion conditions in automotive cylinders to a greater nicety, with greater efficiency in power output and fuel economy.

It is well known that the structure of hydrocarbons profoundly affects the speed of combustion and knocking tendencies. This is clearly brought out in Table 1 which shows the octane ratings of individual hydrocarbons of the paraffin, olefin, cycloparaffin and aromatic series. The effect of hydrocarbon structure on octane rating is clearly shown by the three pentanes which have been studied. Normal pentane has an octane rating of 64, the 2,2-dimethylpropane an oc-

[1] Ipatieff, Corson and Egloff: Ind. Eng. Chem., **27**, 1077 (1935); Ipatieff and Egloff, Paper presented before the American Petroleum Institute Meeting, Tulsa, Okla., May, 1935; Nat. Pet. News, **27**, No. 20, 24g, May 15, 1935; Oil and Gas J., **33**, No. 52, 31, May 16, 1935.

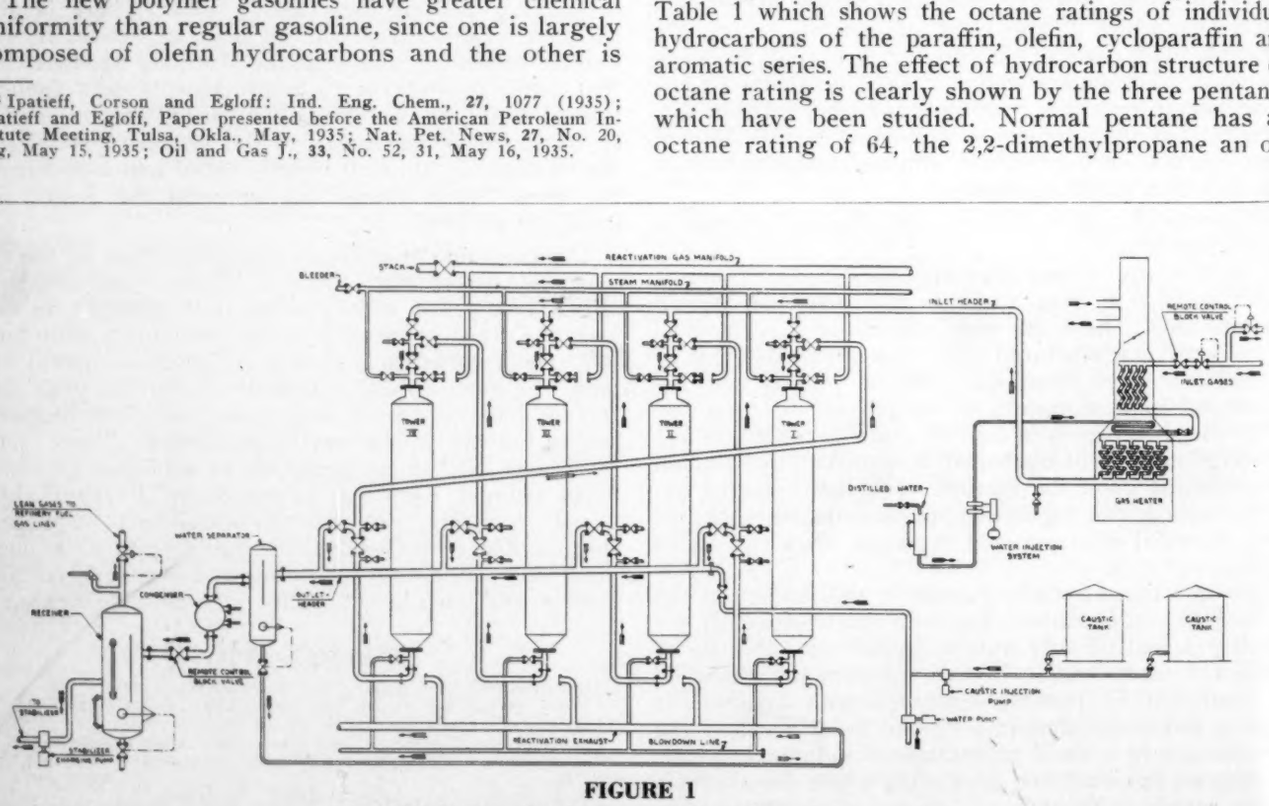
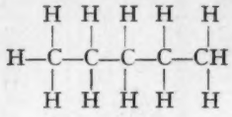


FIGURE 1
Simplified flow chart of a catalytic polymerization unit.

tane rating of 83 and the 2-methylbutane has a value of 90. The structural formulae of the three pentanes and corresponding O. N. ratings are shown as follows:

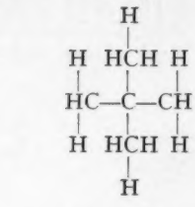
Octane Number

Normal Pentane



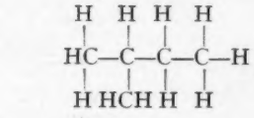
64

2,2-Dimethylpropane



83

2-Methylbutane



90

TABLE 1

Octane Ratings of Hydrocarbons (C.F.R. Motor Method)

	Hydrocarbon Symbol	Octane Number
PARAFFINS		
Methane	CH_4	125 Est.
Ethane	C_2H_6	125 Est.
Propane	C_3H_8	125 Est.
Butane	C_4H_{10}	91
Isobutane	C_4H_{10}	99
Pentane	C_5H_{12}	64
2, 2-Dimethylpropane	C_5H_{12}	83
2-Methylbutane-isopentane	C_5H_{12}	90
Hexane	C_6H_{14}	59
2, 3-Dimethylbutane	C_6H_{14}	95
Heptane	C_7H_{16}	0
Octane	C_8H_{18}	— 0
Iso-octane-2, 2, 4-trimethylpentane	C_8H_{18}	100
Nonane	C_9H_{20}	— 28
Isodecane	$C_{10}H_{12}$	93
Isododecane	$C_{12}H_{26}$	100
OLEFINS		
1-Butene	C_4H_8	80
2-Butene	C_4H_8	83
Isobutene	C_4H_8	87
Di-isobutene (polymer product)	C_8H_{16}	84
Tri-isobutene (polymer product)	$C_{12}H_{24}$	87
Di-isoamylene (polymer product)	$C_{10}H_{20}$	75
CYCLOPARAFFINS		
Methylcyclopentane	C_6H_{12}	82
Cyclohexane	C_6H_{12}	77
AROMATICS		
Benzol	C_6H_6	97
Toluol	C_7H_8	100+

CATALYTIC POLYMERIZATION

The U. O. P. catalytic polymerization unit consists of a heater, catalyst chamber, condenser, receiver, stabilizer and equipment for reactivating the catalyst in situ. Due to the low temperature (450°F.) and pressure (200 pounds) used, the installation cost is relatively low and a number of plants have been built or are designed based upon using old equipment around the refinery such as pressure vessels, etc.

The flow chart (Figures 1 and 2) and photographs illustrate commercial catalytic polymerization units.

The olefin-containing gases are heated to a temperature of about 450°F. and under pressures of the order of 200 pounds, in a furnace from which they flow over the "solid phosphoric acid catalyst" through the catalyst chambers. The flow through the chambers is in series. A combination of the olefins present in the gases takes place. The time, temperature and pressure are so controlled that the products of the catalytic reaction boil within the gasoline range. A small quantity of steam is continuously added to the gases passing through the process which serves to prevent dehydration of the catalyst under the operating conditions. The heat liberated by the polymerization reaction increases the temperature in the catalyst chamber to about 550°F.

The products of the reaction are passed through a condensing coil and the polymer gasoline is drawn from the bottom of the receiver while the lean de-olefinized gas flows from the top of the receiver to mix with refinery fuel gas. The polymer gasoline is pumped to a stabilizer which is so controlled as to produce the vapor pressure product desired. The so-called rich gas from the top of the stabilizer may be further processed by either cracking or dehydrogenation to produce high olefinic gases for re-processing in the catalytic polymerization process.

After continued operation, the catalyst gradually loses its activity which is caused primarily by a deposit of carbonaceous material. To reactivate the catalyst to its original state, the carbonaceous material is removed by oxidation to water and carbon dioxide. The temperature of the oxidation is controlled by passing a stream of combustion gases containing limited percentages of oxygen over the catalyst; the maximum temperature generated in the catalyst bed does not exceed 950°F. The combustion gases entering the catalyst bed are held at a temperature of about 600°F. which is the approximate ignition temperature for the carbonaceous material and oxygen. It is desirable to limit the amount of water vapor in the combustion gases to about 3 percent by volume.

After the oxidation or burning of the carbonaceous material has been completed, it is necessary to hydrate the catalyst to the proper degree so as to produce the highest activity. This is accomplished by maintaining the catalyst in an atmosphere of steam for 10 to 16 hours at approximately 500°F.

GAS ANALYSES

To analyze gases from the cracking process is a relatively complex operation when it is desired to obtain reasonably close results on the individual components present. A quick determination of the total percentage of propene, isobutene, 1-butene and 2-butene present in cracked gases may be made by first passing the gas through a potassium hydroxide gas pipette to remove hydrogen sulfide and carbon dioxide and then through an 87 percent sulfuric acid pipette. The absorption in the latter pipette gives the yield in percent of the 4 olefins. When the isobutene percentage is desired the steps are potassium hydroxide solution as before followed first by absorption in a 64 percent solution of sulfuric acid which polymerizes the isobutene, after which an 87 percent sulfuric acid solution may be used for the determination of the mixture of propene, 1-butene and 2-butene.

Before the design of a catalytic polymerization unit is made, analysis for each component present in the cracked gas is made by a combination of low temperature Podbielniak[2] and Gockel apparatus.[3]

The hydrocarbon gases to be processed catalytically

[2] Ind. Eng. Chem., Anal. Ed., 5, 119 (1933).
[3] Modified by Universal Oil Products Co.

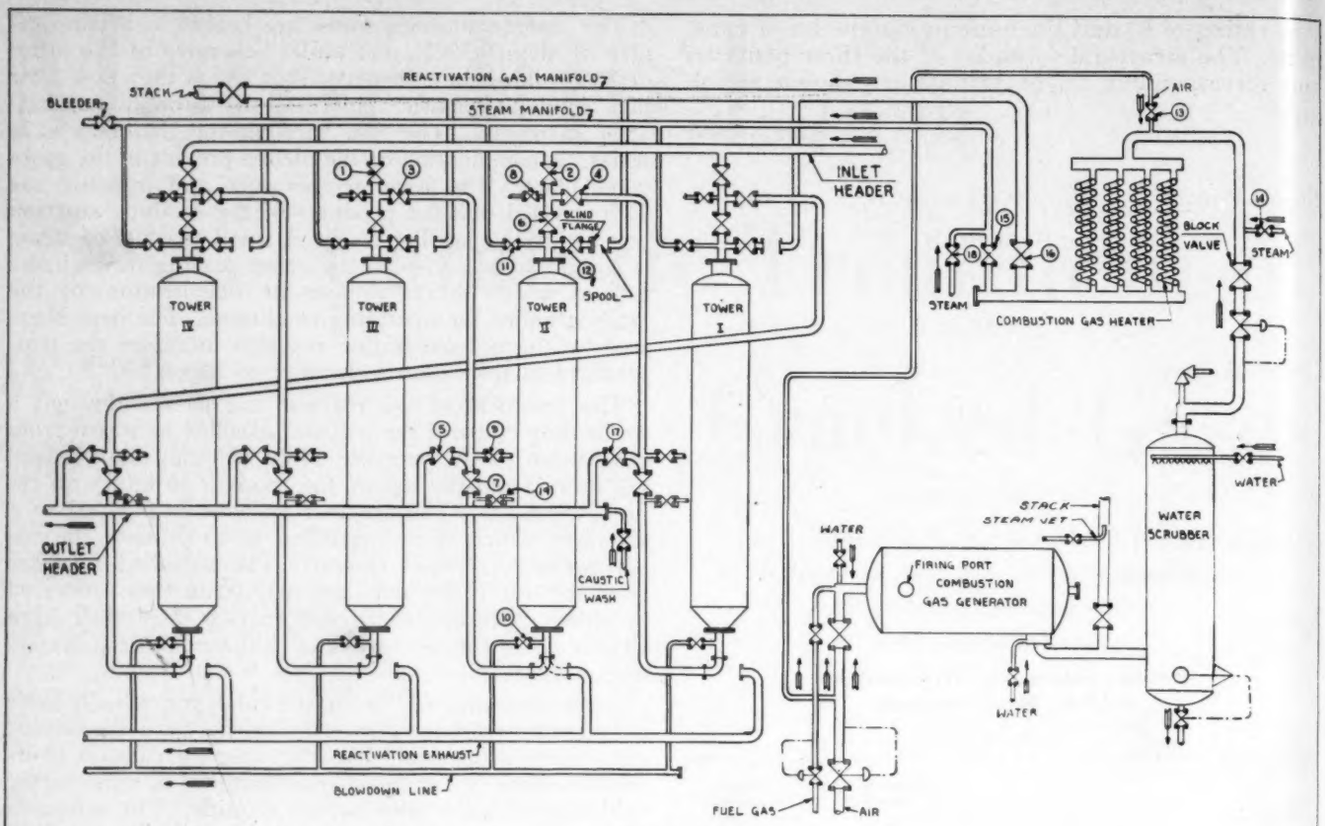


FIGURE 2

Flow chart of the catalytic polymerization unit including the catalyst regenerating procedure.

may vary widely in propene and butene percentages. Typical analyses are shown in Table 2.

TABLE 2

	Stabilizer Gas, Percent			Deeply Stabilized Gas, Percent	Receiver Gas, Percent
Noncondensibles	5.5	4.0	8.6	0.4	26.5
Ethylene	2.9	16.0	2.6	0.6	6.0
Ethane	13.4	17.8	10.4	4.4	17.3
Propene	15.3	29.0	14.0	9.3	11.2
Propane	39.4	22.2	34.4	21.8	26.8
Isobutene	3.8	2.6	4.3	9.5	1.2
n-Butenes	5.9	6.2	6.0	17.6	2.8
Butanes	12.9	2.0	18.2	36.4	5.6
Pentanes and higher	0.9	0.2	1.6	....	0.2
Propene and Butenes	25.0	37.8	24.3	36.4	15.2

Hydrocarbon gases containing olefins such as propene and butenes are derived from the cracking process, the cracking of propane and butane, or their catalytic dehydrogenation into the corresponding propene and butenes.

YIELDS OF POLYMER GASOLINE

The possible yield of polymer gasoline per 1000 cubic feet of olefin-containing gas is a function of the percentage of propene and butene and their ratio. The higher the percentage present, the greater the yield of polymer gasoline. Also the yield of polymer gasoline is larger if more butene than propene is present in the gas.

A number of commercial cracked gases were analyzed for their propene-butenes percentage. The yields of polymer gasoline of 10 pounds Reid vapor pressure derivable per 1000 cubic feet of gas are shown in Table 3.

TABLE 3

Propene and Butenes Percent in Cracked Gas	Polymer Gasoline, Gallons per 1,000 Cubic Feet Cracked Gas
14.1	2.4
17.8	3.0
18.0	3.1
18.9	3.7
21.3	4.2
24.1	4.9
27.1	5.3
27.5	5.8
33.3	7.0
34.3	7.3
41.0	9.2

CATALYTIC POLYMERIZATION UNITS

A number of Universal Oil Products catalytic polymerization units are in commercial operation, under design or course of construction or projected, which range in daily capacity from 600,000 to 27,000,000 cubic feet of cracked gas, with a propene-butene content of from 14 to 41 percent.

The data covering these units is shown in Table 4, relating to cubic feet of cracked gas per day, the percentage of propene and butenes present, the gallons of polymer gasoline per 1000 cubic feet of gas, and the total polymer gasoline per unit per day.

PROPERTIES OF POLYMER GASOLINE

Polymer gasoline has but relatively few hydrocarbons present, which are made up predominantly of olefins. An interesting study of this gasoline was made by Tongberg, Nickels, Laborski and Fenske of Penn State College who reported before the Petroleum Section of the American Chemical Society meeting at Pittsburgh, September 7, 1936, that "the distillations were run in

TABLE 4

Catalytic Polymer Unit Cracked Gas Million Cu. Ft. per Day	Percent Propene-Butenes in the Cracked Gas	Polymer Gasoline Gallons per 1,000 Cu. Ft.	Polymer Gasoline 10-Lb. Reid Vapor Pressure, Gallons per Day
0.6	27.1	5.3	3,180
0.7	33.5	7.1	5,040
1.1	17.7	3.0	3,300
1.8	14.1	2.4	4,230
2.0	24.1	4.9	9,500
3.1	18.0	3.1	9,800
4.2	41.0	9.2	39,000
5.0	17.9	3.0	15,000
6.0	27.5	5.8	34,800
6.7	34.6	7.3	49,200
7.8	21.0	4.2	33,000
8.7	18.9	3.7	32.375
12.5	34.0	7.3	91,200
15.0	33.2	6.8	102,000
27.0	21.6	4.2	113,500
102.2			545,215

a 0.95-inch i.d., 39-foot tall column having approximately 100 theoretical plates under total reflux with a mixture of n-heptane and methylcyclohexane. The charge in each distillation was 10 liters and the average reflux ratio was 40 to 1. Each fraction of distillate corresponded to 0.6 to 1.5 percent by volume of the charge."

"Two very narrow boiling fractions were obtained in the fractionation of polymer gasoline as follows in Table 5:

TABLE 5

Volume Percent of Charge	Boiling Range	Refractive Index Range	Bromine No. Range	A.P.I. Gravity Range
9.3	94.8—95.6	1.4109—1.4112	177—182	65.7—66.6
6.9	97.0—97.8	1.4140—1.4152	188—195	64.1—64.5

Included in the second fraction were 3 small fractions comprising 3.1 percent of the charge, having a boiling point of 97.7-97.8, a constant refractive index of 1.4140, a constant bromine number of 192 and varying in A.P.I. gravity by 0.3. No pure hydrocarbon for which information is available has properties approaching the above.

Hydrocarbons[4] boiling similarly to the 94.8-95.6°C. fraction are shown in Table 6:

TABLE 6

	B. P. ° C.	d_4^{20}	n_D^{20}
Heptene-1	94.9	0.6993	1.3999
Heptene-3	95.9	0.7043	1.4090
3-Ethylpentene-2	94.9	0.7172	1.4120

"Three facts in the polymer gasoline fractionation are outstanding, first that 48.1 percent of the original gasoline could be classified as having 7 carbon atoms, second that bromine numbers were too high for monoolefins, and third that the refractive index curve gave no pronounced peaks and valleys. This last fact indicates that the same type structure predominates and that the aromatic, cyclic olefin, and diolefin content is low. The high bromine numbers are probably due to substitution and not to diolefins. In view of the results, the presence of branched, reactive olefins would be expected."

The percentage distribution of the number of carbon atoms in the hydrocarbon molecules of the fractions in the polymer gasoline are shown in Table 7:

[4] Soday and Boord: J. Am. Chem. Soc., 55, 3293 (1933).

TABLE 7

No. of Carbon Atoms	Polymer Gasoline Volume, Percent
3–4	0.0
5	1.7
6	5.6
7	48.1
8	15.2
9	0.0
10	0.0
11	0.0
11 and higher	12.3*
Loss	17.1†

*Actually this volume contains some hydrocarbons of smaller number of carbon atoms that drained back into the still.

†A sudden leak developed near the still when the distillate temperature reached 125.5° C. This accounts for the major part of the loss.

Polymer gasoline is particularly outstanding in its octane rating and blending value. The product coming from the catalytic polymerizing unit boils within the gasoline range. Depending upon the hydrogen sulphide present in the cracked gas, the percentage of sulphur in the polymer product may be low or high. The hydrogen sulphide may be removed from the cracked gas by one of a number of commercial processes. Hydrogen sulphide reacts with the olefins present in the cracked gas producing mercaptans, which can be almost entirely removed by strong caustic soda.

A stabilized cracked gas containing 0.8 percent hydrogen sulphide yielded a polymer gasoline containing 0.63 percent sulphur whereas after scrubbing the gas with caustic soda the polymer gasoline contained 0.02 percent sulphur. The data of the polymer products are shown in Table 8.

TABLE 8
Polymer Gasoline (as produced)

	Unscrubbed Gas		Hydrogen Sulphide Removed
A.P.I. Gravity	69.5	66.5	67.2
Gum (Atlantic Refining Co. Method, Copper Dish (mg.)	23	36	51
Sulphur, Total, Percent	0.63	0.31	0.02
Mercaptan Sulphur, Percent	0.48	.....	0.00
Octane Number (C.F.R. Method)	82	79	82
Oxidation Bomb Induction Period, Min.	90	.....	45
Reid Vapor Pressure	12.8	.....	10.6

100 C.C. A.S.T.M. DISTILLATION

Initial B.P. ° F.	89	94
Percent distilled over:		
10	140	158
20	169	186
30	192	199
40	204	207
50	214	215
60	227	224
70	245	241
80	289	277
90	355	333
End Point	415	415

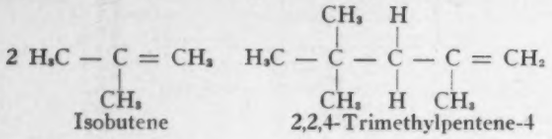
The blending valve of polymer gasoline varies as a function of the gasoline to which it is added. When starting with a 44-octane gasoline, the rating of octane is raised to 59 using a 20 percent polymer gasoline concentration, whereas when the starting gasoline was of 70-octane rating, it was raised to 74 when using the same concentration as shown in Table 9.

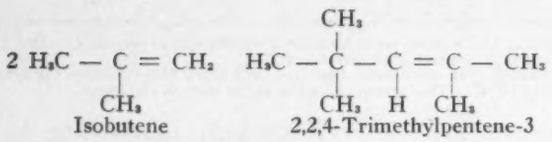
TABLE 9

Percent 81-Octane Polymer Gasoline Added	OCTANE RATINGS OF BLENDS	
	44-Octane Straight-Run Gasoline	70-Octane Regular Gasoline
5	48	72
10	52	73
15	56	74
20	59	74

The production of 95-100-octane fuel can be brought about through the catalytic polymerization of the isobu-

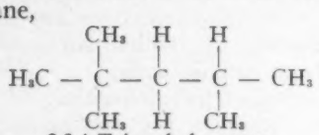
tene present in cracked gases. A mixture of 2,2,4-trimethylpentene-3 and 2,2,4-trimethylpentene-4 is technically known as "di-isobutene."





The octane rating of "di-isobutene" by the C.F.R. Motor Method is 84, but on a blending value basis in Reference Fuel A-3 of octane rating 44, the octane rating ranges from 153 to 95 in concentrations from 5 to 75 percent.

Upon mild hydrogenation the two trimethylpentenes comprising di-isobutene form the same iso-octane, 2,2,4-trimethylpentane,



of 95-100 octane number. The properties of the fuel are 71 A.P.I. gravity and a boiling range of 206-244°F. The maximum concentrations of the butenes in cracked gases are those derived from the liquid condensate in the stabilizer composed of butanes and butenes. The percentage composition varies widely, dependent upon the stock which is cracked, as shown in Table 10.

The iso-octane produced from the hydrogenation of di-isobutene is readily blended with isopentane[5]. It is stated that "Isopentane can be added in considerable proportions in the manufacture of high octane number ing the supply of such gasolines relative to the supply of iso-octane. Isopentane imparts desirable volatility to the iso-octane blends. From the antiknock viewpoint, isopentane has a value ranging from 92 to 100 percent of that of iso-octane in making 100-octane number aviation gasoline."

Over a billion gallons of 95-100 octane motor fuel can be produced yearly in the United States from the present hydrocarbon gases available, and this volume can be increased markedly whenever the economic demand is present.

Another eight billion gallons of polymer gasoline are potentially available from gases dissolved in crude oil, from cracked gases, and the propane-butanes supply of natural gas.

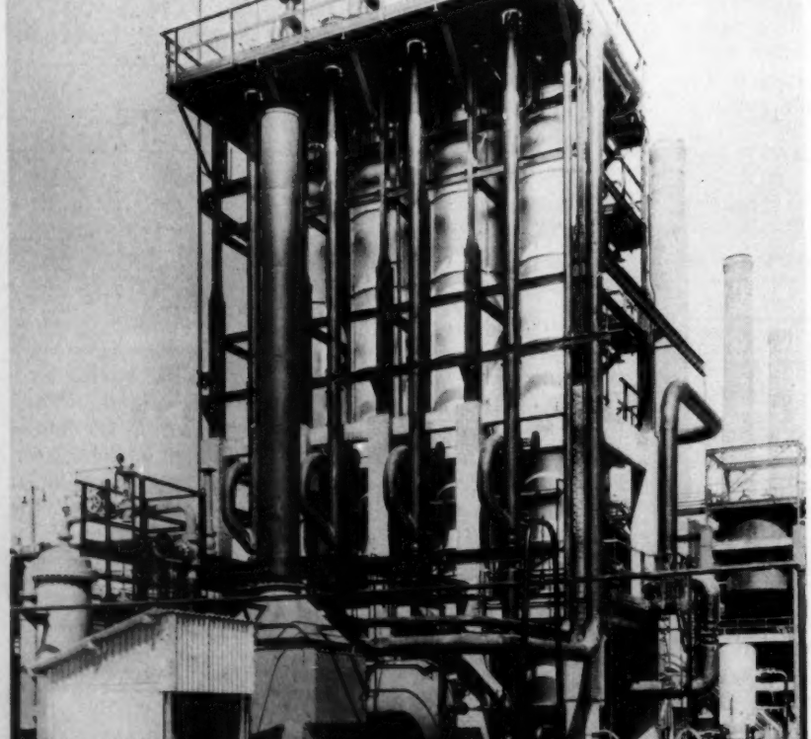
TABLE 10

Butenes and Butanes from Stabilizers
Percent by Volume

Number	1	2	3
Isobutene	8.9	11.5	12.4
n-Butenes	19.3	36.1	28.7
Butanes	68.4	52.4	58.9

[5] Neptune, Trimble and Alden, Oil and Gas J., p. 26, April 23, 1936.

aviation gasolines. It has the effect of greatly augment-



Catalytic polymerization unit with capacity of 8,000,000 cubic feet of gas daily.

The Wiggins

Balloon Systems

JOHN H. WIGGINS

Presented before the Manufacturing Section of the Western Petroleum Refiners Association

THE storage and transportation of volatile and explosive oils is a "process" which must be in operation 24 hours of each day. A "process" is a means of effecting a result comprising the control of physical or chemical laws. Until recent years in the minds of most oil men the problem of oil storage has been a mechanical job to get done.

When petroleum executives and engineers come to a full realization that it is a "process" and that the machinery for effecting results requires constant supervision, then in a few years the fire and explosion hazard and the evaporation loss will be brought close to an economic minimum.

The distillation and cracking of oils into gasoline and other products are *processes.* Many other operations in the refinery are *processes.*

The factors normally placed under control by these processes are: a. the force of gravity; b. temperature; c. pressure; d. chemical changes; e. volumetric expansion; f. friction.

During the development of refining processes, these factors were recognized and studied and placed under greater and greater control about in the order in which they are enumerated. The results of such development have been a tremendous improvement in the products and the cost of production.

In handling and storing oil we have all of the above enumerated factors to consider. In the case of refining processes we use and vary these factors one or more at once in order to improve the products and decrease their cost. In the case of transportation and storage, we find ourselves in an entirely different position. We are now in a position of defense. The gasoline and crude oil must be defended against the inroads of these very same factors.

The history of transportation and storage shows that up to about 15 years ago, the only factors given much consideration were the force of gravity and friction. The result of neglecting the other factors was tremendous losses in percentage of the volatile products, which at the same time lowered the quality.

Along about 1921, the oil industry began to grow conscious of this fact. The first of the factors partially controlled was temperature; next, pressure, and volumetric expansion.

At first it was a general belief among executives and some engineers that evaporation losses could be reduced only partially. They thought there must occur a considerable loss in any container. The developments of the present time, however, refute that idea. As a theoretical proposition, evaporation losses can be entirely eliminated if the correct process is applied to the problem at hand. It can be done on an economical basis, also. As a business proposition, it may not always be best to stop all loss, but practically all loss can be stopped with financial and material advantage. In most cases the price of gasoline cannot get so low that it will not pay to stop evaporation for the simple reason that the system to stop the loss will pay for itself at a price per gallon which is far below the cost of producing gasoline.

A great many devices and materials have been developed and used which have decreased evaporation and fire losses. This paper describes the balloon system only.

The complete balloon system consists of:

1. The balloon.
2. Special vent valves at the balloon.
3. Vapor lines interconnecting the storage or working tanks and the balloon.
4. Tank fittings, comprising, a. gastite vent valves set at a pressure higher than the venting pressure of the balloon; b. special gauging and sampling device; c. manometer for correcting gauge readings.
5. Supply of gas to the balloon with valve automatically operated by the balloon.

The balloon system involves not only a process but also a device which is a very low pressure, all steel, dry gas-holder having no "seal." It depends for its change of volume upon the slight flexing of two steel diaphragms. This device is called a "balloon" for the reason that this word best describes its operation. The development of this balloon has been the most important part of the development of the whole system.

To bring the balloon system for the prevention of evaporation and fire in oil and gasoline tanks to its present state of development has taken about seven years. The important features of this development will be noted for the purpose of a better understanding of the finished product.

The first experimental balloon was built in 1929 at Okmulgee, Oklahoma. It was designed to determine something about the amount of pitch that could be given the top diaphragm without risking failure due to excessive flexing. In a 50-foot diameter diaphragm, a pitch of 36 inches in 15 feet of radius was built. This was quite evidently too great, even though it had completely flexible areas for relief. It did operate, however, but was abandoned without putting it into service.

Another problem in connection with this whole process is to keep the pressure on the cone-roofed storage tanks as low as possible for several reasons. Therefore, the next balloon was built with the idea of determining

whether this type of structure could be built of very thin galvanized plates. Hence, in 1930, a 90-foot diameter, 22,000 cubic foot commercial installation was made, using 22-gauge galvanized steel sheets. These were only 1/32-inch thick.

A hook seam, with cement and a small rivet at about 6-inch spacing was used. A pitch of 18 inches in 20 feet of radius was built into the upper and lower diaphragms, which was in the range of experience with the breather roof. This structure operated successfully for several years connected to one 55,000-barrel gasoline tank. Though this type structure could be built in this manner if sufficient care and expertness were used, it was deemed too difficult for a production specification.

Between 1930 and 1932 several experimental balloons were built to test various types of design and methods of construction.

In the spring of 1933 a 128-foot diameter, 100,000 cubic foot balloon was built which had a 16-gauge welded steel top and a 14-gauge welded steel bottom. This structure also embodied the principle of flexing the peripheral portion of the bottom and operating the balloon throughout its whole range of volume under a slight pressure. (Some of the early balloons had operated for a part of their volumetric range under a slight vacuum). It was determined from this structure that 16-gauge could be successfully welded and would operate. But again, for a production job 16-gauge was believed to be too thin.

In 1933 and 1934, four large balloons and a small one were built, ranging up to 350,000 cubic feet capacity, having 14 diaphragms and 11 shells. During the building and operation of all these balloon systems it became evident the extremely low pressures—namely, from ⅜-inch to 1 inch of water—which had been striven for—were not necessary if all the tanks connected to the system were really gastite and had the proper fittings for their operation.

Therefore the balloons built in 1935 and thereafter had 11-gauge diaphragms, both top and bottom. With this weight of metal it is easy and practicable under regular conditions of steel plate construction to get a good welded job. The working pressure range is from 1 inch to 1⅝ inches of water. This higher pressure is just about equal to the weight of a 3/16-inch plate cone roof.

When the balloon is full and venting the cone roof is not quite lifted off its rafters and hence no strain is placed upon it. In this connection it may be pointed out that the balloon is always lower than the tops of the tanks and hence the vapor column, which is heavier than air, throws a pressure varying from ⅛-inch to ¾-inch of water, depending on the richness of the vapor and the net height of the vapor column. Thus the entire pressure thrown by the balloon is not applied at cone roof.

Nothing has been said about technical details and principles involved in the design and operation of the balloon. It should be stated, however, that the venting mechanism for both pressure and vacuum is operated by the balloon diaphragms, which give tremendous power for operation. Thus they can be designed so that they are gastite and stay gastite, but still will open when necessary even though the seat may have ice on it.

An enumeration of the parts of the balloon as it is built today for balloon systems is as follows:

An 11 steel welded top diaphragm sloping downwardly toward the center.

An 11 steel welded bottom built on an earth grade shaped so that the peripheral portion of the steel bottom slopes upwardly until it meets the top and then slopes downwardly toward the center in such manner as to support the top when the balloon is empty.

A vertical shell which joins the peripheries of the top and bottom diaphragms.

Compression girders at the top and bottom of the shell.

Counterweights attached to the shell equal to the weight of the shell and a portion of the bottom diaphragm.

Devices placed on the top diaphragm which completely control its shape at every state of filling or emptying.

A single valve for both pressure and vacuum relief, actuated by the movement of the balloon during normal operation.

A double automatic siphon drainage system at the center.

A volumetric recording device is optional.

Special vent valves at balloon.

In order that the balloon itself, as well as the tankage, may be made completely safe against failure under any circumstances, such as accidentally blinding the balloon so that it had no vents or an excessive temporary snow load or a cloudburst, which would accumulate a great load of water, the balloon is equipped with an emergency valve which is sealed by a mixture of glycerine and water. It is so designed that it cannot be clogged or sealed shut in any manner. It should be so installed on the balloon that it can never be blinded. One or more of these valves placed along the vapor lines is a very cheap safeguard against pulling in tanks by sudden vacuum or by failure of tank vents to operate due to sticking. In a normal operating system these emergency valves never open.

VAPOR LINES

The principal problem is to get large diameter lines installed at a low cost. Standard type pipe with thick walls costs too much, for the two-fold reason that the pipe itself has a high cost and, secondly, the cost of the support and installation is high. Thus, thin-walled pipe was adopted.

One of the early installations had a pipe of special design, being made up in the field. It was of 22 galvanized iron, octagonal in cross-section, with a special cast iron ring for the joint, and a hooked and soldered seam. It worked out satisfactorily, the main objection being that special tools and technique were necessary to manufacture it. The final result has been to buy all pipe ready fabricated, or to roll it in the shop and weld all seams in the field. All fittings are cut and welded in the field. The gauge used is from 14 to 11. Using such light pipe makes it possible to use very light angle iron supports in concrete bases at from 30 feet to 40 feet centers. The pipe is placed just above ground or as high as local circumstances demand. If possible the pipe is maintained in a hydraulic gradient from tank to balloon. In any case an automatic siphon drain is placed at each low point so that liquid will never fill the pipe. Ordinarily the vapor line is connected to the tank at one of the existing openings. Such connections are made without taking the tank out of service.

Provision is made so that any or all tanks can be shut off from the balloon system.

Vent Valves. At present any standard make of vent valves can be used on the tanks. These must be set at a pressure which is in excess of that at which the balloon vents, since all venting (if there is any) should be controlled by the movement of the balloon diaphragms.

Gauging. It is preferable to use a gauge well which

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Present Day Tendencies in
Petroleum Cracking

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CRACKING, has probably become the most important single operation in petroleum refining. Even a sketchy consideration of the subject is impossible in a paper of the size and scope of this one. It is therefore necessary to limit our field to the cracking practice best fitted to serve this particular locality. In attempting to do this, we would like to set forth a few general characteristics of this area which have a bearing on refining and more particularly on cracking.

In the first place, topped crude is the most commonly available charging stock. There are, of course, instances of gas oil cracking and also of reforming. Since time is limited, we shall deal primarily with cracking plant design for operation on topped crude, bearing in mind that a well designed cracking unit for this purpose can be applied to the handling of lighter stocks when such need arises.

In the second place, refinery locations in this area at times were chosen more with an eye to crude supply than to markets. Many refiners in these parts have developed a considerable local market which is served by tank truck delivery and several refiners have access to gasoline pipelines, but by and large, the average refiner must find a distant market served by tank car delivery. This fact makes it imperative that the quality of the gasoline produced be equal to or better than the competitive products available in these distant markets. There is always a considerable market for a lower grade product at a reduced price. But this is not good business for the refiner, since high quality products that will sell for top prices can be produced with modern equipment at a cost no greater than the present cost of the lower grade products.

Since, as above stated, the primary market of the average refiner of this area is rather distant from the point of manufacture, it is necessary that the cost of the product be kept low in order that these distant markets may be served at a profit. If the production cost can be lowered without sacrifice of quality, this advantage may be taken as an additional profit. But even more important is the fact that with a lower cost quality product, the marketing area can be increased from any given refinery location. In view of the present clash for marketing territory, this point is of major importance.

We dare not forget that a refinery is a commercial institution, and without profits it cannot exist. Neither can we overlook the fact that the first cost of a unit affects the operating cost since fixed charges are inescapable in setting up cost figures. And these fixed charges are substantially in direct ratio to the first cost of the unit. However, there is certainly no sound reason behind attempts to cut first cost of cracking plants by cheapening the construction. Keeping the first cost down can better be accomplished by simplification of detail and by use of newer types of equipment which are entirely satisfactory for the purpose but which cost less to fabricate or erect. In short, we believe it sound to place emphasis on better engineering rather than on cheap equipment in order to reduce plant costs.

In order to be specific, we shall discuss features of one particular type of cracking unit in its relation to the older types and shall also attempt to correlate trends in design with benefits to be derived from resultant changes.

The tube furnace or heater is rightfully considered the most important piece of equipment in a cracking unit. There is not time to attempt to trace the development of heaters. Suffice it to say that most of the early tube furnaces applied to the cracking art were of the convection type, wherein combustion was completed in one compartment, following which the combustion gases were led over a bridge wall and downward through a convection bank and thence to the stack. Then came radiant tube sections.

In the early furnaces and even today in many, the radiant tubes were or are disposed along the walls, roof or floor (or all three) of the compartment which in convection furnaces was used for combustion only. Gas flow is still downward through the convection tube bank. This was a natural development for the time, since many furnaces were originally built for convection banks only, and later, radiant tubes were added, these being placed near the walls and roof of the combustion chamber. But certain disadvantages are inherent in this type of furnace. Principally, they are:

First, the normal flow of flame and combustion gas is horizontal, then vertical, then horizontal again, and finally downward. Such a flow is not easily directed. There results flame impingement and hot spots, with consequent coking troubles and oxidation of tubes.

Second, cold spots are present, especially in or near corners of the rectangular combustion chamber, resulting in loss of effectiveness as a heater and in extreme cases, the deposition of coke due to cooling of oil on the way through the furnace.

Third, because of flame impingement troubles, the combustion chamber is of necessity made large. The resultant heater is expensive to build.

In the meantime, at least one company interested in cracking plant development, built experimental heaters from which were obtained results both surprising and gratifying. These experimental heaters proved beyond any reasonable doubt that much higher heat input to radiant tubes could be satisfactorily achieved if flame and gas travel were better controlled and also, if walls,

flame, and tubes were more favorably disposed one to the other. Out of this experimental work, plus a lot of field experience, grew a furnace of a new type.

In this furnace, the flame and combustion gas flow are entirely upward, first along both sides of a centrally located bridge wall and thence upward through the convection bank. Radiant tubes are arranged along the side walls, opposite the flame and bridge wall, the latter acting as radiator. Tubes also bridge over the top of the combustion space. The convection bank continues upward. Stack gases are collected by a breeching and led to a conventional stack. As will be noted, the travel of flame and resultant combustion gases, is substantially in a straight line upward.

This arrangement avoids hot spots, cold spots and flame impingment and makes possible high heat input to the tubes without operating difficulties. And perhaps surprisingly enough, it is distinctly a low cost heater.

Two rows of burners are present, one alongside each side of the bridge wall. When desired, the coil can be arranged so that a controlled heating curve can be had, since the furnace is effectively divided into two separate combustion chambers, each with its own set of burners and radiant tubes.

A controlled heating curve is particularly desirable when cracking gas oil or lighter materials, as for instance, in the light oil furnace operation of a two coil unit. On the other hand, the upshot furnace design also permits arranging the tubes in two parallel coils. This is especially desirable when cracking heavy oil, since it effectively reduces the time of passage of oil through the coils.

Two-coil cracking has just been mentioned. Of course, any reasonable number of coils can be used but we have in mind a unit of moderate cost. In two-coil operation, the feed to the furnaces is fractionated into a gas oil of about 26 gravity and a heavier oil of say 20 gravity. Each is subjected to the most favorable temperature pressure conditions for the particular type of stock. This results in a distinct improvement in octane number of the gasoline. As a sample, one two-coil unit is producing from Kansas top-bed crude a 400 endpoint gasoline of 69 octane. Another 68 to 69 octane. Operators of very large cracking units can profitably consider three-coil or even four-coil installations but the two-coil unit is ideal for moderate sized refineries. Multicoil cracking may be considered one of the distinct trends at this time, largely because of the higher octane gasoline produced thereby.

Another distinct trend that has been under way for several years and is still gaining favor, is the full cracking of the raw feed by putting it in its entirety through the furnace. In the earlier days of cracking means of preventing coking difficulties were not as well worked out as at present. Hence there was the tendency among operators to go the easier way and discard the heavier portion of the raw feed without putting it through the furnace coil. This was conducive to prevention of coking troubles with their consequent forced shut downs. But the penalty was and still is heavy.

In the first place, the fuel oil or residuum thus produced is a high viscosity, high cold test product which in many instances is not readily marketable. Viscosity breakers have in many instances been installed to overcome the difficulty but this is expensive and complicates the plant unnecessarily.

In the second place, yields of gasoline are distinctly lower when the whole oil is not cracked. Estimates on this point vary but our observation is that plants that do not put the whole oil through the coil, yield 5 to 10 percent less gasoline of a given end point. This percentage is based on net throughput of the unit.

In view of the foregoing, it is obvious that the difference in results obtained by not cracking or by cracking the whole raw feed are very considerable. In the meantime, knowledge of controlling coke formation has been developed so that today a multitude of cracking units are showing the better results of total cracking and are at the same time giving very satisfactory length of runs.

Another tendency in cracking operation is toward the use of a reaction chamber, rather than a soaking bank. This is in a sense a corollary of heavy oil cracking. Now of course, reaction chambers are as old in use as cracking plants, but we have in mind a later form as applied to recent units.

A soaking bank works rather satisfactorily with certain gas oils and lighter charging stocks. But its use becomes almost impossible when heavy oils are cracked, because of coking difficulties in the tubes. In our opinion, the best present day practice for heavy oil cracking, consists of very high velocity short time factor treatment in the heavy oil coil. Following this the total products therefrom (without reduction of pressure or temperature other than normal losses) are led immediately to a reaction chamber so disposed that liquid products are quickly discharged while vapor products are held for a longer time. The combined effects of these methods are:

First, the short time element and high velocity in furnace coil by maintaining an intimate mixture within the tubes, prevents coke formation or over-cracking.

Second, heavy oils are quickly ejected from the reaction chamber, thus preventing overcracking of these less refractory hydrocarbons.

Third, the lighter hydrocarbons are retained for a predetermined time period, during which time, cracking continues. This time period can be adjusted to the needs of a particular stock by adjusting the pressure on the chamber. In a very real sense, a reaction chamber of this type becomes an aid to selective cracking.

Another tendency in present day cracking is toward intermediate pressures in the main fractionating column. There is not time to discuss properly the function of fractionation in a cracking plant. But such a discussion is rather unnecessary anyway, since nearly everyone involved in the operation of refinery units has a pretty fair knowledge of their function.

Fractionators (ofttimes referred to merely as bubble towers) in various units that have come to our notice, have been operated in some instances as low as 20 pounds gauge pressure and in others as high as 300 pounds. In our opinion, best practice lays between 70 pounds on the low edge and 120 pounds as the upper limit.

There is considerable difference in charging stocks, and other conditions enter in, so that there will probably always be some divergence on this point. But with pressures distinctly below the above range, the size of the fractionator, flash chamber and condensers all become rather large and therefore expensive. But more serious is the fact that loss of light products is much more serious at lower condenser and fractionating pressures.

Of course, practically all cracking plants are now equipped with vapor recovery units. Even so, this latter part of the plant is of necessity more elaborate and expensive when the cracking plant fractionator is operated at decidedly low pressures. Low fractionator pressures also increase circulating pump loads by lowering pump suction pressure, and increase furnace load by decreasing oil temperature to the furnace.

On the other hand, too high fractionator pressures quickly lead into trouble. First, because higher pressures automatically carry with them higher temperatures. The latter ultimately reach a point where coking occurs in the fractionating system, particularly in the flash chamber (or evaporator).

Second, as above mentioned, temperatures increase in the vessels involved as pressures are increased, but not rapidly enough to overcome the tendency for gasoline to remain in the feed to the furnace or furnaces. This latter results in reduced plant capacity on one hand and low gasoline yields and high losses on the other.

Third, for the same reason, the flash point of the residuum may be too low if too much pressure is carried on the fractionating equipment.

In this connection we mention briefly a practice that is favored by many. The residuum is flashed in a secondary chamber and reduced to a low gravity and high viscosity. Resulting gas oil from this flash is returned to the cracking cycle. The low gravity residuum is cut back to marketable specification by light oil from the cycle. An increase in gasoline yield results. It may be questioned whether this increase justifies the cost and complication in the case of very small units. Larger units can profitably follow this scheme.

Pumping units for furnace oil circulation are of prime importance. Several well established types and makes are available but it is not within the scope of this discussion to cover this matter. However, we should like to mention briefly the prime movers for these units.

Originally, hot oil circulating pumps were direct driven steam pumps, either duplex or simplex. Then followed cross compound duplex pumps. Later came crank and flywheel steam driven pumps, quite often with vacuum condensers. This latter type of pumping unit is still quite commonly used. Steam turbine or electric motor driven centrifugal pumps, gas engine driven and Diesel driven power pumps complete the list.

So many considerations enter into choice of pump drive that it is impossible to generalize too much. We may say, however, that for this area, steam is coming into some disfavor. The first cost of a steam driven unit is always high if boilers are taken into account. Aside from this is the fact that water conditions are generally bad and boiler maintenance is no small problem.

Electric drive is expensive in operation, especially when current is purchased from the outside. Gas engine drive is moderate in first cost, low in operating cost, but lacks just a little in reliability, because refinery gas presents difficulty making it advisable to purchase gas from the outside, which in turn makes the unit liable to trouble from outside fuel difficulties. However, if a thoroughly reliable source of natural gas is available, gas engine drive is satisfactory.

In our opinion, Diesel drive is about the most satisfactory for general use. It is moderately expensive, but very reliable, very moderate in operating cost and is operated on fuel produced by the cracking plant itself. Therefore, it is not subject to outside fuel difficulties.

For purposes of fuel cost comparisons, let us assume 150 hydraulic horsepower load to drive hot oil pumps of a moderate sized cracking plant:

First, assume an electric driven power pump with current at ⅞ cent per K.W. hour. This computes to $1.25 per hour or $900.00 per month.

Second, assume a crank and flywheel unit with condenser, having a steam duty of 20 pounds. Assume firing boilers with 1000 B.t.u. gas valued at 10 cents per thousand, or fuel oil at 60 cents per barrel, and charging for the fuel only. This computes to 58 cents per hour, or $417.00 per month. This includes no charge for boiler maintenance.

Direct driven steam pumps will cost from three to five times the above.

Third, assume Diesel drive using gas oil at 3 cents per gallon. This computes to 34 cents per hour or $245 per month.

Fourth, assume gas engine drive using 1000 B.t.u. gas and 13 feet per H.P. hour. This computes to 24 cents per hour or $168 per month.

The above figures may vary depending on constants chosen, but the comparison is fair.

One of the more recent improvements in cracking plant design has been the change to open type condensing and cooling units. By open type, we mean tubular sections of the type which are set above a pit and over which cooling water is sprayed or otherwise distrbuted. Submerged sections set in a box, although much used, are not entirely satisfactory because even when fairly new and clean, the transfer rate is low. Worse, however, is the fact that scale and dirt collect rapidly, thus rendering the unit ineffective. Because of being installed in a box, cleaning the tubes is difficult and such cleaning can only be done while the unit is shut down and the boxes drained. The net result is that they are seldom cleaned and the streams are often warm or hot. Open sections operate at a much higher transfer rate. Less surface is required and the first cost of the plant is lowered appreciably. Equally important is the fact that the scale can be removed much more easily, thus minimizing warm stream difficulty and loss.

While open spray sections have been in wide use for several years in the natural gasoline industry, nevertheless the refining industry has been slow to adopt them. Part of this is natural resistance to change. But more of it is the feeling that in case of a water supply failure, the water in the box around the submerged coils will serve to prevent a serious situation arising due to escape of uncondensed vapors. This matter, however, can be handled by a water reservoir back of the spray system, or by tying in city water where same is available, or by duplicate water pumping equipment. Many open type coolers and condensers are in successful refinery operation and their use is coming into favor.

Vapor recovery and stabilization is no small part of a cracking unit. A few years ago, cracking plants were built without including such equipment. The result was a severe loss of the best gasoline hydrocarbons, amounting to as much as 10 percent of all the gasoline produced by the cracking plant. Several points of octane rating were lost as a consequence. At the same time, the gasoline was not properly stabilized, that is, it still contained propane in solution.

During this period, vapor recovery plants as separate units were widely installed and in most cases were quite satisfactory and proved to be excellent investments. These earlier plants were for the most part an adaptation of natural gasoline oil absorption plant designs. A number of compression and direct fractionating units were also installed. These were a descendant of the German Blau gas patent stabilizer.

More recently, however, cracking plant and vapor recovery plant engineers have gotten closer together with the result that both cracking plant and vapor recovery plant have been modified so that the two can be more conveniently tied together. This results in a much simpler, lower cost and more satisfactory combined unit than was heretofore possible. At present, almost all

cracking units are designed and built with vapor recovery and stabilization equipment included.

In these later recovery units, heat for stabilization is taken from the cracking cycle by circulating hot oil through the reboiler or reboilers. Absorption is practiced in order to prevent loss of pentane and heavier with cracked gas. Absorption menstruum in one form of unit is a naphtha which in reality is the heaviest third of the cracked gasoline itself. In another type of unit, absorption menstruum may be either gas oil from the cycle, or cold raw feed. Stabilization is properly performed so that finished product is commonly propane free, and with butane content so controlled that the cracked gasoline leaves the unit at required vapor pressure for shipment.

In the average refinery there is produced by cracking, more butane than can be retained in the finished cracked gasoline. But in the average sized refinery, this excess butane is not available in sufficient quantity to justify marketing it separately or using it for gas cracking or reforming. However, generally speaking, a good deal of this butane can be added to the straight run gasoline.

In certain areas and particularly in Kansas, this method of butane conservation has not been feasible because of color instability when a small volume of cracked gasoline and a larger volume of straight run gasoline are blended. At the present time there is at least one treating process coming to the fore, by use of which this difficulty is apparently overcome.

Blending excess light cracked hydrocarbons into straight run gasoline as a means of increasing cracking plant yields, has been practiced in several Mid-Continent refineries for several years. But none of them are in this district for reasons above stated. One Kansas refiner is equipped to do so, as soon as treating difficulties are overcome.

At this time, polymerization of unsaturated compounds (principally olefins) present in cracking still gas bids fair to become the next important development in the cracking art. One or two processes are now available to large refiners but it can scarcely be said that the art has been perfected to the point where a moderate sized unit can be profitably operated. We believe that within the next year or two, details of processing will be improved to the point where smaller refineries will find it profitable to polymerize their gas.

The value of polymerization lies in part in the fact that additional gasoline is produced from gas that is now used as fuel, but the larger value of the process lies in the fact that the gasoline so produced has an extremely high octane rating and an even higher blending power, so that a small amount of gasoline so produced can be used to raise the octane number of all the cracked gasoline. Polymerization practice is developing along two principal lines. One process utilizes a catalyst and operates at relatively low pressures and temperatures. Other processes use very much higher pressure and temperature, but no catalyst.

In the design of cracking units to meet present day requirements, one principal requirement not heretofore mentioned, is flexibility in operation.

Flexibility in a cracking plant can probably best be achieved, not by adding gadgets Christmas tree fashion, but rather by sound processing and by equipment capable of overload in regard to capacity, pressure and temperature, so that operating conditions can be varied to meet changing requirements.

The Wiggins Balloon Systems

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reaches to within about one foot of the tank bottom. This device makes a fool-proof condition. The gauger cannot allow any vapor to escape. A manometer is read in conjunction with the tape reading to get a correct result. Automatic gauges are also good where it is permissible to use these.

Sampling. The best sampling device is a number of small diameter pipes placed at various elevations, projecting about three to five feet inwardly from the shell and terminating at the bottom of the tank on the outside, where a control valve is placed. If it is impracticable to install these, a second thief hatch cover is placed inside the existing one. This allows sampling with a very small amount of vapor loss, since this second cover is kept closed while running the cord through a small slot.

Make-up Gas. No matter how large the balloon, within reason, there will be times when it is empty and will then have to take in either air or some other gas. It is better to take in a permanent dry gas other than air. Thus in a short time all the air and therefore practically all the water vapor will be eliminated from the system. The benefits from this condition are principally two: first, the entire system cannot explode or catch fire internally even by spontaneous combustion because there is no oxygen present; second, the internal corrosion of balloon, piping and tankage will be very much decreased since not only is oxygen absent but also water vapor is decreased to the point where it will not condense.

Dry, permanent sweet gas should be piped to the balloon, where it can be used for make-up when necessary. It is allowed to flow into the balloon system through a valve which is operated by the balloon diaphragm just before the balloon becomes empty.

Maintaining the entire vapor space of the balloon system free of water and oxygen is one of the important assets of the entire process. It tends to make it fire safe and corrosion free.

A properly designed balloon system will stop practically all evaporation loss from both working and storage tanks. In the case of working tank losses, there should be a sufficiently large group of tanks so that the pumpings come somewhere near balancing. Depending upon the size of the plant, this figure may be from a few thousand gallons to several thousand barrels per day.